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MEASUREMENT OF AMBIENT AMMONIA
CONCENTRATIONS IN SOUTHERN CALIFORNIA

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FINAL REPORT

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Rockwell InternationalEnvironmental Monitoring & Services Center
Environmental & Energy Systems Division**ABSTRACT**

Four analytical methods for the determination of ambient ammonia concentrations were evaluated, both in the laboratory and in the field. One method was chosen for additional field study, improvements were made, and field measurements were conducted at five sites in the South Coast Air Basin over a one-year period. The improved method utilized a specially constructed sampling system containing a Teflon prefilter to remove particulates followed by oxalic acid impregnated filters to trap ammonia gas. The overall precision of the sampling and analytical method, including random error associated with the localized source, was found to be about ± 3 ppb. During the course of the study, measured ammonia concentrations ranged from less than 1 ppb in West Los Angeles to more than 50 ppb in Riverside. Annual averages for West Los Angeles, El Monte, Long Beach, Santa Ana Canyon, and Riverside were 1.81, 4.00, 5.07, 8.23, and 12.11 ppb, respectively. From the relationship between



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1.0 INTRODUCTION

The concentration of gaseous ammonia is a very important atmospheric chemical parameter affecting both the physical and chemical nature of several species. The neutralization of acid gases by gaseous ammonia results in the formation of aerosols which usually impair the visibility in the atmosphere. In addition to neutralization the basic character of ammonia also affects very extensively redox reactions of gaseous and particulate atmospheric species. It is therefore very important to understand better the sources and the concentrations of ammonia in the atmosphere, especially now that the ammonia injection process may be introduced as a means of reducing the oxides of nitrogen emission from stationary sources.

The measurement of ambient ammonia concentrations has received very early attention and several analytical methods were developed for this. One of the measurement techniques utilized impingers containing dilute solutions of sulfuric acid for sampling ammonia in the air. This method utilized by Junge to determine the background concentration of ammonia. In Scandinavia the background was found to contain 2.9 to 7.2 ppb ammonia, along the coast of Florida it was 3.2 to 11.5 ppb ammonia and in Massachusetts, the ammonia concentration ranged from 4.8 to 20 ppb(1). Breeding, et al(2), measured ammonia using impingers at sampling sites located in rural areas of Missouri and Illinois, upwind from major anthropogenic sources. In the periods of 1971 and 1972, the average ammonia concentration was 4.2 ppb. In these initial measurements, the background ammonia concentration was found to be uniformly distributed throughout the world. Maximum ammonia concentrations in the northern hemisphere occurred during the summer.

The collection efficiency of impingers for ammonia was investigated by Okita and Kanamori (3). High concentrations of ammonia (greater than 1 ppm) collected for 15 minutes resulted in quantitative collection. However, lower concentrations, sampled for longer time periods, resulted in reduced collection



efficiencies with some as low as 40%. The flow rate used in these experiments was 1.5 liter/min. Sakimoto and Miyazaki (4) found that the collection efficiency of impingers increased with increasing flow rate, possibly due to turbulent mixing. At a flow rate of 3 liter/min, they achieved approximately 100% collection of ammonia for concentrations above 40 ppb.

Healy, et al (5), made consecutive one-hour measurements for ammonia at Harwell, England, by collecting samples on No. 2 porosity sintered glass plates treated with sulfuric acid at flow rates of 30 to 40 liters/min. These measurements took place from May through September 1969, and measured an average ammonia concentration of 2.4 ± 1.5 ppb. Additionally, a significant diurnal variability in the ammonia concentration, in which the concentration at night was higher than during the day, was observed. Healy ascribed this the diurnal variation in the mixing height resulting in higher values at night.

Okita and Kanomori (3) used glass fiber filters impregnated with sulfuric acid to collect ammonia gas. They obtained 95% collection efficiency with a 15 liter/min flow rate at relative humidity in the range of 39 to 47%. Work performed at the EMSC (6), has shown that at humidities greater than 80%, the hygroscopic nature of sulfuric acid results in blockage of some of the flow channels through the filters resulting in a decrease in the flow rate.

Shendrikar and Lodge (7), at the National Center for Atmospheric Research, used filters impregnated with oxalic acid to collect ambient ammonia. In their experiments they observed 100% collection efficiency at a flow rate of 4 liter/min and relative humidities of 0% to 30%. This method was then used to measure atmospheric ammonia in Colorado in February and March 1974. The average concentration measured was 4.6 ± 0.8 ppb, however, particulate ammonium was not removed from the sample flow prior to the collection with the acid treated filters.



Numerous optical methods have been developed recently which are adaptable to the measurement of ammonia. Ammonia can be converted to NO by stainless steel or platinum at temperatures near 800°C, and the NO can be analyzed by the chemiluminescence method (Breitenbach and Shelef, (8) ; and Baumgardner, McClenny and Stevens (9)). A laser adsorption spectrometer employing a wavelength tunable diode laser has been described which can measure in real time ammonia concentrations with sensitivities better than 0.1 ppb (Reid et al.(10)). Richmond, et al (11) have used an opto-acoustic technique to detect ammonia. In this method, CO₂ laser radiation is absorbed by the ammonia, and is converted to kinetic energy. The laser output is chopped so that the corresponding variation in air pressure caused by the ammonia absorption is picked up by a microphone and electronically converted to a voltage which is proportional to the ammonia concentration. These devices are expensive and are not easily applied to large-scale field programs. However, McClenny and Bennett (12) at EPA, have found that ammonia is readily adsorbed onto Teflon beads. The ammonia can then be thermally desorbed into any of the above-described detectors with the total amount of ammonia recovered being proportional to the electronic signal integrated with time.

Based on the measurements of ammonia in the atmosphere described above, background ammonia concentrations generally were found in the 2 to 20 ppb range, with a high probability that the concentration will be less than 6 ppb. It has been estimated that 99.9% of this ammonia is produced by biological processes (Miner (13), Junge (14)), primarily due to decomposition of organic waste matter. Removal of ammonia from the atmosphere is achieved to a large extent by the oceans, where the equilibrium between gaseous ammonia and dissolved ammonia is on the order of 1.4 to 2.9 times the atmospheric concentration.

Industrial and urban sources of ammonia include all types of combustion, oil refining, fertilizer plants and organic chemical process plants. Ammonia releases from combustion processes are listed in Table 1-1 (Hovey, et al. (15)).



The role of ammonia on air quality has been studied by various investigators. Ammonia appears to play an important role in the formation and stabilization of secondary aerosols. The rate of heterogeneous oxidation of SO_2 in the presence of particulate is strongly dependent on pH (Junge (1)). As the aerosol droplets become more acidic, the reaction rate becomes slower and at very low pH it practically stops. The introduction of ammonia neutralizes the acid and also forms a buffer which allow much larger quantities of SO_2 to be oxidized to sulfate (Freiberg (16)).

Formation of nitrates from oxides of nitrogen is hypothesized to be strongly dependent on the ammonia concentration. Orel and Seinfeld (7) predicted that an increase in ambient ammonia concentration from 10 to 50 ppb results in a 2.3 times increase in nitrate formation. Essentially, what can be visualized as occurring in the South Coast Air Basin initially, is a system containing primary gaseous and particulate pollutants along with background gases (NO , NO_2 , O_3 , SO_2 , $\text{SO}_4^{=}$, NO_3^- water vapor, NH_3 , etc.). NO and NO_2 are oxidized to nitric acid by homogeneous and/or heterogeneous mechanisms. Interaction between the nitric acid, oxides of nitrogen, and ammonia increases the net production of nitrate. These particles, containing dissolved NO , NO_2 , and nitric acid, have a very low pH for heterogeneous formation of sulfate so that nitrate formation continues in preference to the oxidation of SO_2 ; until the ammonia, nitric acid, ammonium nitrate system approaches equilibrium (Stelson, Friedlander, and Seinfeld (18)), at which time the buffering action of the dissolved ammonia facilitates the oxidation of SO_2 . The role of nitrate and sulfate particulates on visibility reduction has been characterized and studies indicate that nitrate particulates are the primary contributors to visibility reduction (Grosjean and Friedlander (19)). Therefore, high ammonia concentrations can result in increased formation of nitrates initially, followed by increasing the sulfate formation with the net effect of reducing the visibility in the South Coast Air Basin. Healy, et al. (5), found high correlation between ammonium in particulates and the decrease in visibility. In these aerosols the ammonium to nitrate and ammonium to sulfate molar ratio indicate that these species to a large extent exist as NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$.



TABLE 1-1

Ammonia Emissions from Combustion (Hovey, et al (14))

<u>Source</u>	<u>Amount</u>
Gasoline engines	2.0 lbs/1,000 gallons
Diesel engines	2.0 lbs/1,000 gallons
Coal	2.0 lbs/ton
Fuel oil	1.0 lb/1,000 gallons
Natural gas	0.3-0.56 lb/10 ⁶ ft ³
Butane	1.7 lbs/10 ⁶ ft ³
Propane	1.3 lbs/10 ⁶ ft ³
Wood	2.4 lbs/ton
Forest fires	0.3 lb/ton
Domestic gas heating	0.3 lb/100,000 persons



2.0 METHODS EVALUATION

Based on the currently available information, four ambient ammonia measurement methods were chosen and evaluated for accuracy, precision and freedom from interferences. The four methods are:

- 1) glass fiber filter impregnated with oxalic acid,
- 2) impingers containing 0.1 N sulfuric acid solution,
- 3) glass tubes coated with oxalic acid, and
- 4) adsorption onto Teflon beads.

The reference method for the determination of the accuracy of these ammonia monitoring methods was long-path infrared absorption.

2.1 AMMONIA GENERATION

To evaluate the various measurement methods, standard ammonia atmospheres were generated by diluting the output of a permeation tube in a flow system. A schematic of the dilution apparatus is given in Figure 2-1. The flow of compressed air is controlled with needle valves (V) and monitored by electronic mass flow meters (MFM). The humidity is controlled by proportioning the dilution air with ball valves (Vp) through a humidifier, and the humidity is measured with a dew point hygrometer. The flow rates listed in Figure 2-1 are to generate a concentration of approximately 20 ppb ammonia. Ammonia concentrations of 5 to 200 ppb are generated in this manner. The ability to generate known ammonia concentrations was verified by analyzing the output of the ammonia generator with a chemiluminescent detector coupled with a high-temperature stainless steel converter (Baumgardner et al. (9)). The results of this analysis appear in Figure 2-2 and show that ammonia concentration generated by a permeation tube can be determined by this method to within $\pm 7\%$.

2.2 OXALIC ACID IMPREGNATED FILTER METHOD

The method utilizing oxalic acid filters developed by Shendrikar and

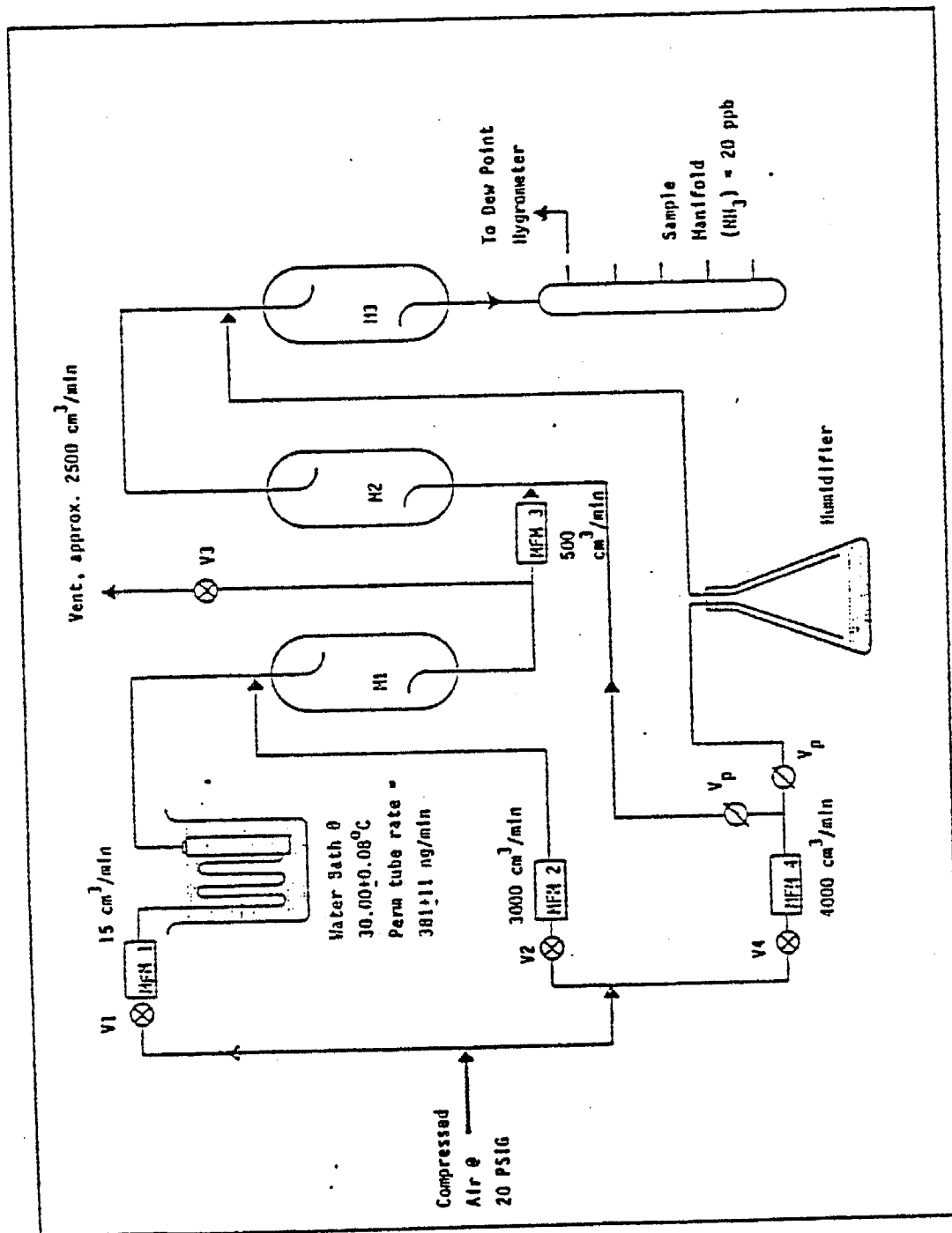


Figure 2-1. Flow Diagram of the Ammonia Generation and Dilution Apparatus

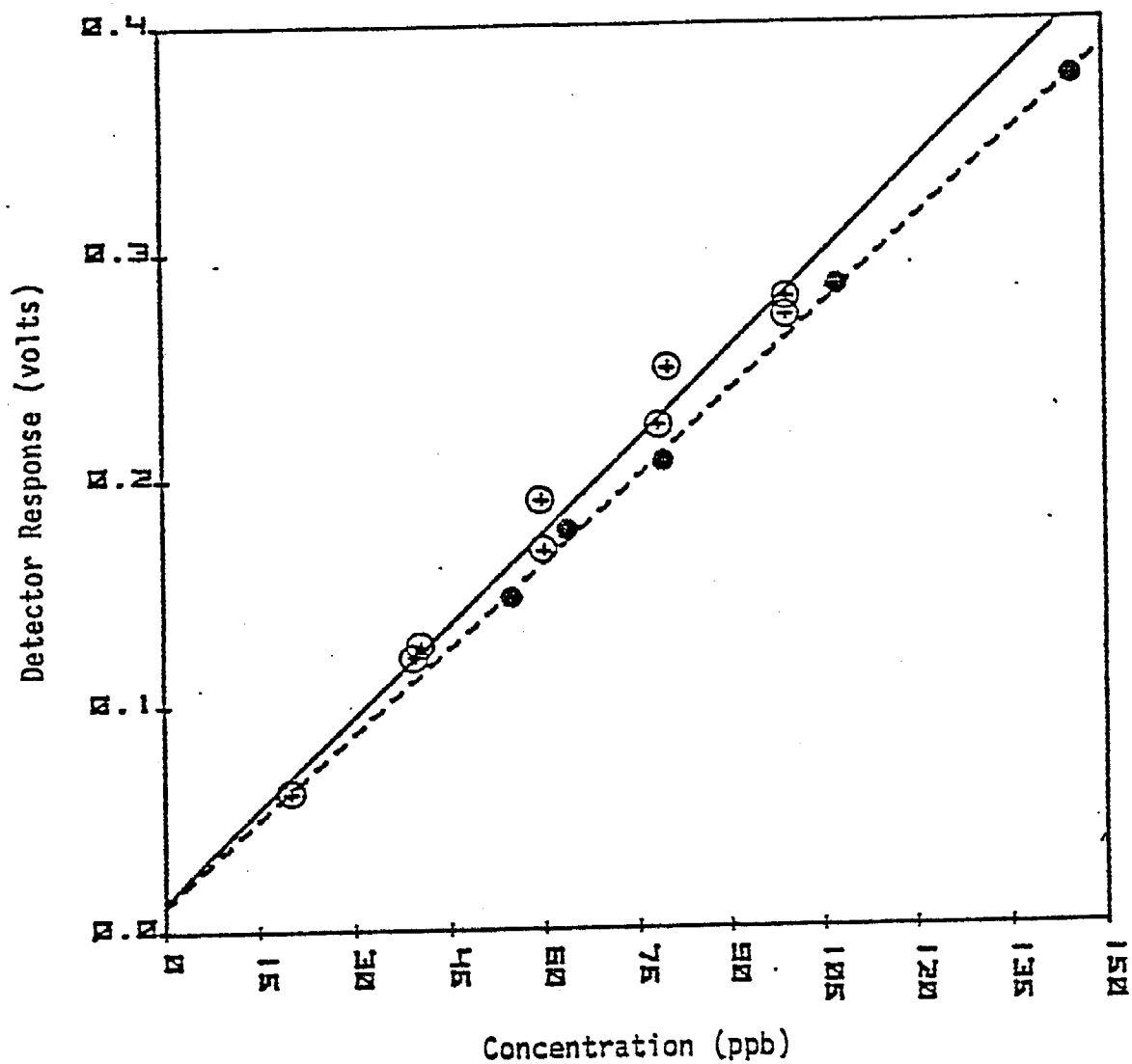


Figure 2-2 Calibration of a Chemiluminescent detector with both NO and NH₃



Lodge (7) was reduced to practice at the EMSC. Glass fiber filters (Gelman type A, 47mm dia) were impregnated with 1 ml of 5% oxalic acid in ethanol (w/v) and allowed to dry under vacuum for approximately two hours. Then they were sealed in individual plastic petri dishes and stored in plastic zip lock bags in which additional oxalic acid was present to prevent their contamination by NH_3 . Oxalic acid has a considerable vapor pressure at room temperature. It is estimated that this vapor pressure is ten times the partial pressure of ammonia at a concentration of 20 ppb so that any ammonia in the vicinity of the filters will be removed by the oxalic acid vapors. Exposure consists of sampling through two filters in series at the rate of 20 liters/min. A prefilter was also used to remove any particulates. The quantitative collection and analysis of ambient ammonia were demonstrated with this method by sampling standard atmospheres generated from a permeation tube and by comparison with ammonia concentrations determined with by this method to these obtained by FT-LPIR as shown in Figure 2-3). The exposed filters were extracted into a 0.0056 M acetate buffer (pH=4.5) and analyzed spectrophotometrically by the Berthelot reaction. The data obtained from this are also discussed in conjunction with the diffusion denuder experiments (Section 2.6).

2.3 BUBBLER METHOD

Bubblers were evaluated for quantitative collection by sampling with two units side by side from the output of the ammonia generation and dilution device. Each unit consisted of two impingers connected in series, with each impinger containing 25 ml of 0.1 N sulfuric acid. By operating the impingers in series, it is possible to estimate the collection efficiency of each individual bubbler. Ammonia concentrations of 5 to 40 ppb were generated and the bubblers were exposed for 6 hours at each concentration. Each day one unexposed bubbler was sealed and set aside to be used as a blank. Both the blank and sample impingers were analyzed for ammonium by the Berthelot colorimetric method. The overall precision of the ammonia measurements with the bubblers is dependent on the consistency of the blank levels. In this set of measurements, the blank solutions remained relatively constant at 1.21 ± 0.1 ppb NH_3 . Results of the experiments with bubblers are presented in Table 2-1. The relative standard deviation as a function of the measured concentration and

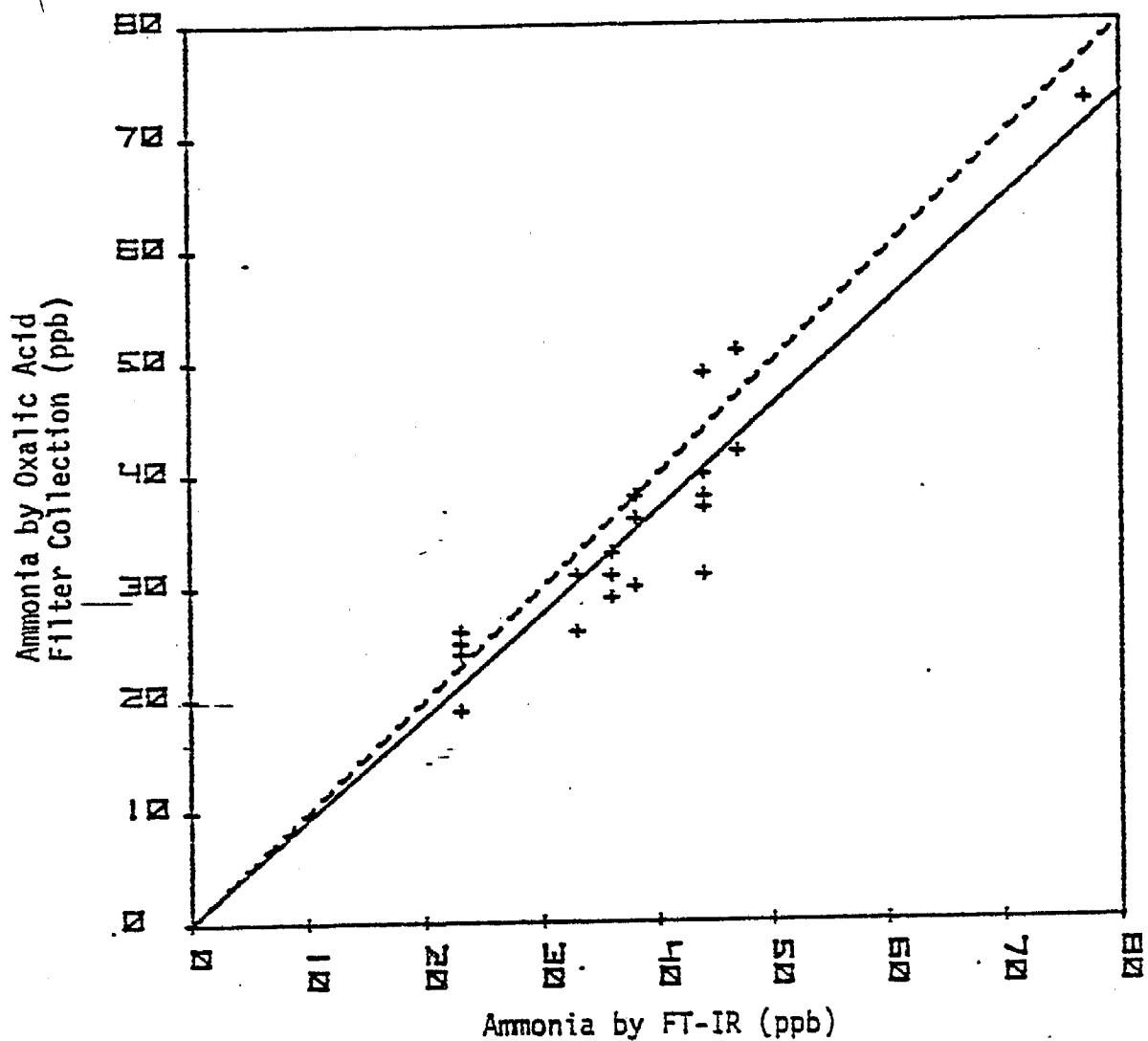


Figure 2-3. Comparison of the ammonia concentration measured by collection with oxalic acid impregnated filters with the concentration measured with Fourier Transform long pathlength infra-red spectroscopy (Richards and Johnson, 1979). The broken line represents the ideal correlation.



Table 2-1

Results of the Collection of Ammonia Generated from a
Permeation Tube by Impingers Containing
25 ml of 0.1 N Sulfuric Acid

Generated Concentration (ppb)	Sample Flowrate (l/m)	Sample Time (min)	Measured Concentration by first impinger only (ppb)	Collection Efficiency*
41.1	0.402	360	34.1	0.83
41.1	0.356	360	35.8	0.87
20.1	0.852	360	16.5	0.82
20.1	1.007	360	15.7	0.78
10.1	1.292	353	8.8	0.87
5.1	1.128	360	3.5	0.69
5.1	1.223	360	4.1	0.81

* Collection efficiency is defined as the fraction of ammonia collected by a single impinger at a given flowrate.



the correlation of the measured concentration with the generated concentration, are presented in Figures 2-4 and 2-5.

The average collection efficiency defined as the fraction of ammonia collected by a single bubbler at a given flowrate is 0.81 ± 0.06 . This result appears to be satisfactory since the use of two impingers in series will collect about 96% of the gaseous ammonia.

This method was also used for the determination of ambient ammonia concentrations. However, the average blank obtained by analyzing unexposed bubblers was about the same magnitude as that of the samples and therefore the actual values could not be established.

2.4 DIFFUSION DENUDE METHOD

With the oxalic acid and bubbler methods, the sample air must first be drawn through an inert filter to remove the particulates. Otherwise, ammonium in the aerosol will contribute to the ammonium concentration in the oxalic acid filters or in the bubbler solution. Inert prefilter is also a likely source of interferences since acidic particles on the prefilter can trap some ammonia. Also, basic particles can release ammonia. In the diffusion denuder method, air is drawn through oxalic acid coated tubes sufficiently slowly so that the gas has the time to diffuse into the wall coating and yet rapidly enough that appreciable quantities of the aerosol do not have time to be

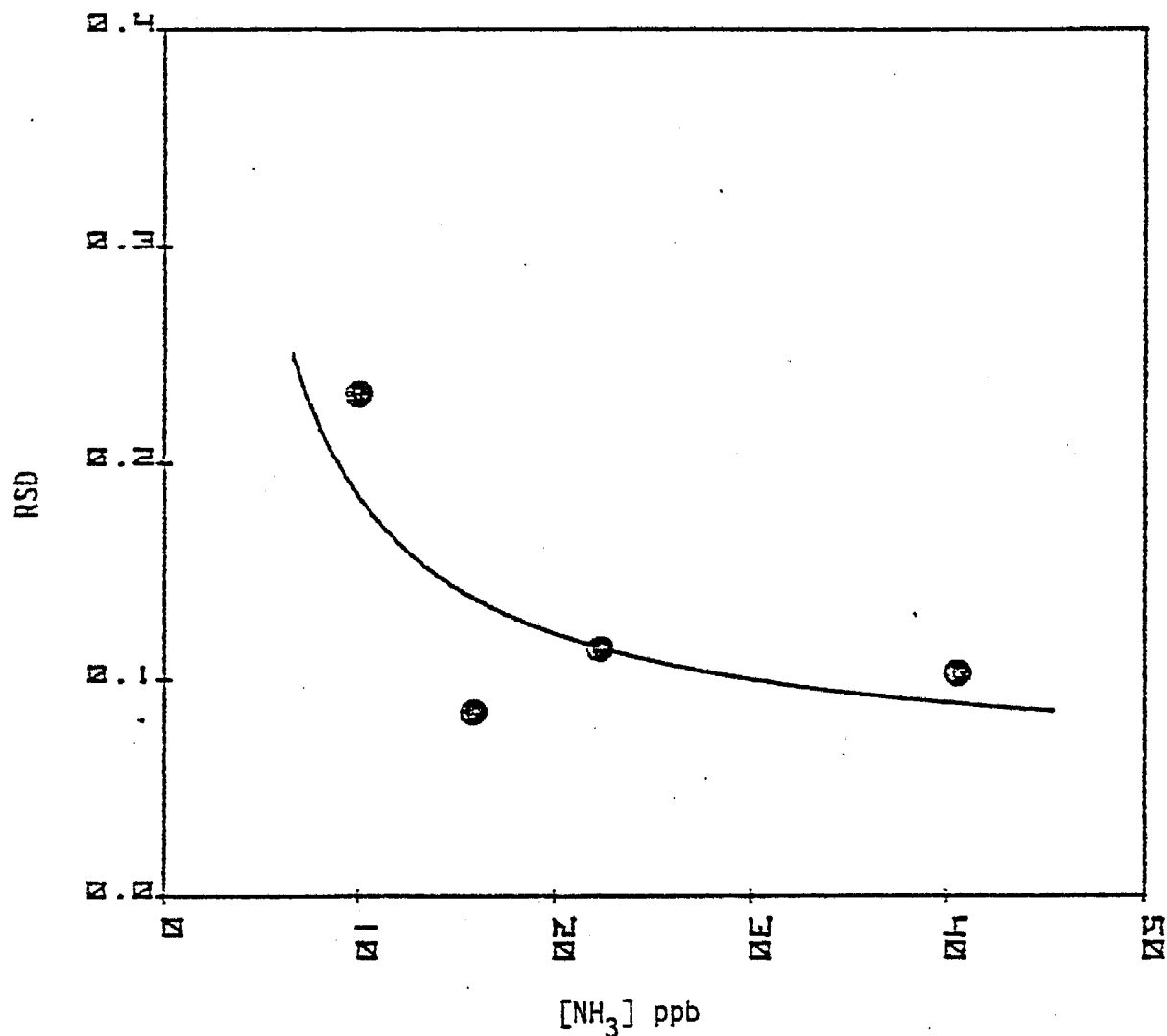


Figure 2-4. Relative standard deviation as a function of the average ammonia concentration determined by the bubbler method. Data are obtained with two sampling trains operating side by side. The curve is represented by the equation: $RSD = 1.27/[NH_3] + 0.057$

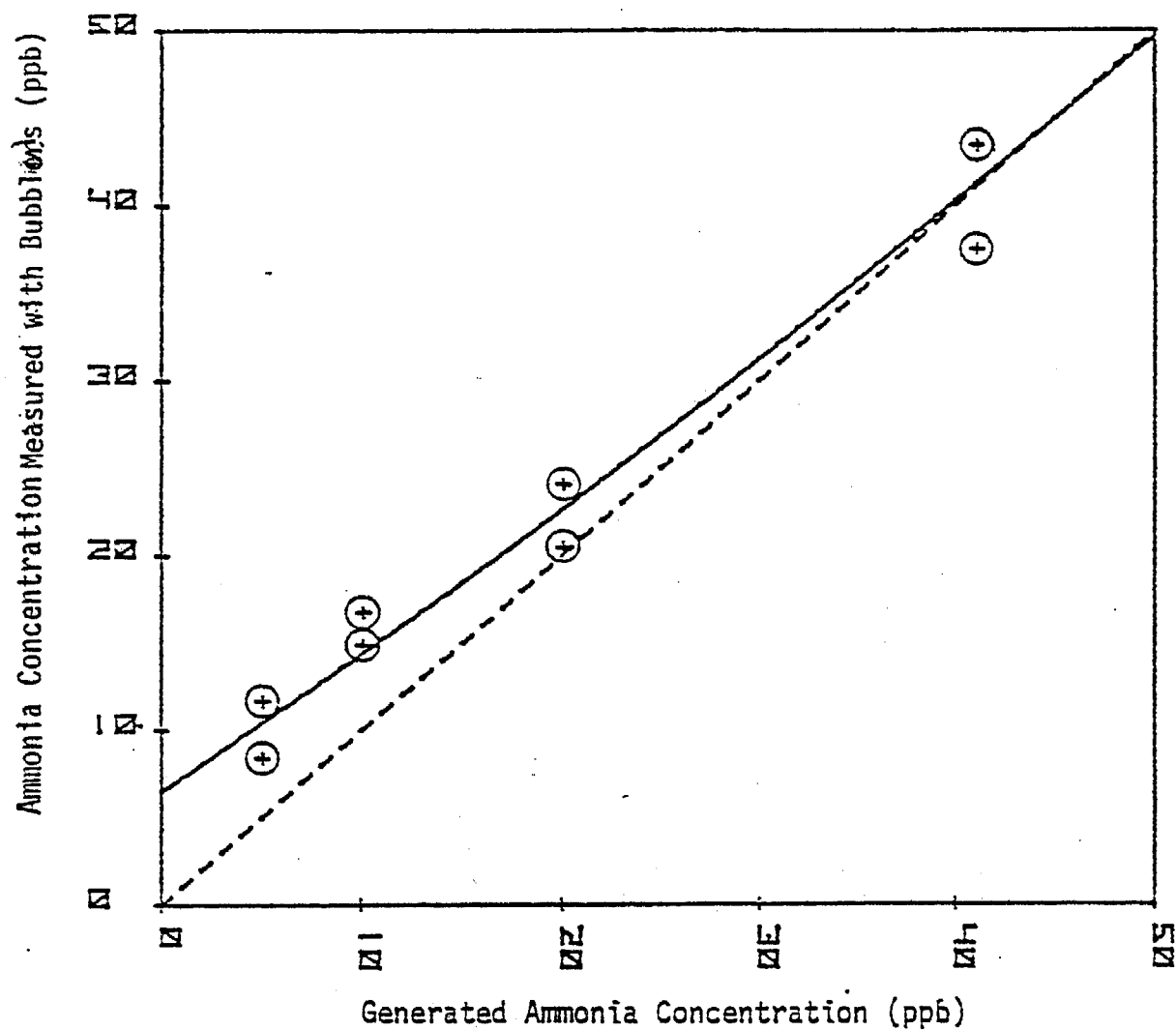


Figure 2-5. Ammonia concentrations determined by the bubbler method compared to the concentration generated with a permeation tube and diluted in a flow system. The broken line represents the ideal correlation.



collected. This is possible because the diffusion coefficient of ammonia molecules is about 10^4 times larger than the diffusion coefficient of the smallest particles which contain significant atmospheric concentrations of ammonium. Diffusion denuders to quantitatively measure ammonia have been used by Brosset (20) with reasonable success. The theory of mass transfer by diffusion from a fluid flowing in a cylindrical tube has been worked out by many investigators. Thomas (21) obtained empirically a five term equation which relates the fraction of particles penetrating the tube to the dimensionless parameter " α ":

$$\frac{\bar{c}}{C_0} = \sum_{n=0}^4 C_n \exp(-\lambda_n^2 \alpha) \quad (A)$$

where

$\frac{\bar{c}}{C_0}$ = the fraction of particles penetrating the tube

$\alpha = \pi D l / q$

D = particle diffusion coefficient cm^2/sec

l = length of tube, cm

q = volume flow rate per tube, cm^3/sec

C_n and λ_n^2 are constants given in Table 2-2

\bar{c} = concentration of particles penetrating the tube

C_0 = concentration of particles entering the tube

n = term in the equation



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TABLE 2-2

Values of the Constants in Equation (A) (Thomas (21))

n	C_n	λ_n^2
0	0.819	3.65
1	0.097	22.3
2	0.032	57
3	0.027	123
4	0.025	750



A diffusion coefficient of $0.22 \text{ cm}^2/\text{sec}$ (Thomas, (22); Andrews, (23)) has been given for ammonia. This, along with a tube 24 cm in length operating at a flowrate of $500 \text{ cm}^3/\text{min}$, should theoretically collect more than 99.9% of the ammonia.

This method of collecting ammonia is desirable because it does not require the use of a prefilter. Particulates, which have diffusion coefficients orders of magnitude lower than the gas molecules, practically will not be deposited on the surface of the tubes. This removes the concern that the filter, or deposits on the filter, will adsorb or release any ammonia.

The diffusion tubes were prepared by coating the inside surface of 1 24-cm long 0.5-cm-ID glass tube with a 5% solution of oxalic acid in ethanol. Initial experiments using these tubes to sample the output of the ammonia generator resulted in collection efficiencies of less than 25%. These experiments were repeated, using tubes coated with 15% oxalic acid in ethanol in series with two oxalic acid filters so that the ammonia which is not collected by the denuder could be determined. Measurements were made at flowrates of 0.67 and 4.7 liter/min at ammonia concentrations of 150 to 200 ppb. Mass balances (i.e., measured conc/generated conc) for these concentrations were on the order of 0.91 ± 0.11 . The difference between the measured collection efficiency and the calculated collection efficiency may be an indication that not all the ammonia molecules which are in contact with the tube surfaces are trapped. However, two tubes in series, each with a collection efficiency of 86%, should result in almost quantitative (98%) collection.

2.5 AMMONIA ABSORPTION METHOD

The fourth method investigated was the adsorption of ammonia onto Teflon, followed by thermal desorption, conversion of ammonia to NO , and measurement by chemiluminescence (McClenny and Bennett (12)). The collection



tubes were prepared by placing approximately 0.5 gms of Chromosorb T (Analabs, 30/60 mesh) in a glass tube 12.5 cm by 0.5 cm ID. The Chromosorb T was held in place by quartz wool plugs. Initial experiments verified McClenny's results, that for sample times of 10 minutes, at a flowrate of 0.2 liters/min, collection efficiency is essentially 100%.

Desorption of the ammonia was achieved by heating the tube to a temperature of approximately 100°C while passing zero air through the tube and into a thermal converter. The thermal converter used is a commercially available stainless steel converter (Thermo Electron Corporation, Model #4006) heated to a temperature of 800°C. According to the manufacturer, at this temperature, the conversion of NH_3 to NO is virtually 100%.

The chemiluminescent detector of a Monitor Labs Model 8440, was modified to increase the sensitivity of NO detection (Steffenson and Stedman (24)). This was accomplished by decreasing the absolute pressure in the reaction chamber and increasing the amount of ozone by reducing the flowrate through the ozonizer. The instrument response as a function of pressure is shown in Figure 2-7. The pressure was measured downstream of the reactor and does not take into account the pressure drop due to the 1/4-inch-OD tubing and the activated charcoal scrubber. With these modifications, it was estimated that the sensitivity of response was increased by a factor of 3.2.

Teflon does not adsorb NO or NO_2 so that these compounds do not interfere in this analysis. Assuming that the desorption efficiency is 100%, an integrated response of 10 volt-sec should be quantifiable (Richards and Johnson (6)). The steady-state voltage associated with this 3-minute integration was 0.056 volts. The chemiluminescent detector, modified for enhanced sensitivity, has a response of 20.4 volts per ppm NO or NH_3 , which converts the above steady-state voltage to 2.7 ppb. The NO detector draws sample air at a rate of 200 cm^3/min , so that 2.7 ppb at this flowrate for 3 minutes is equivalent to 1.1 ng ammonia.

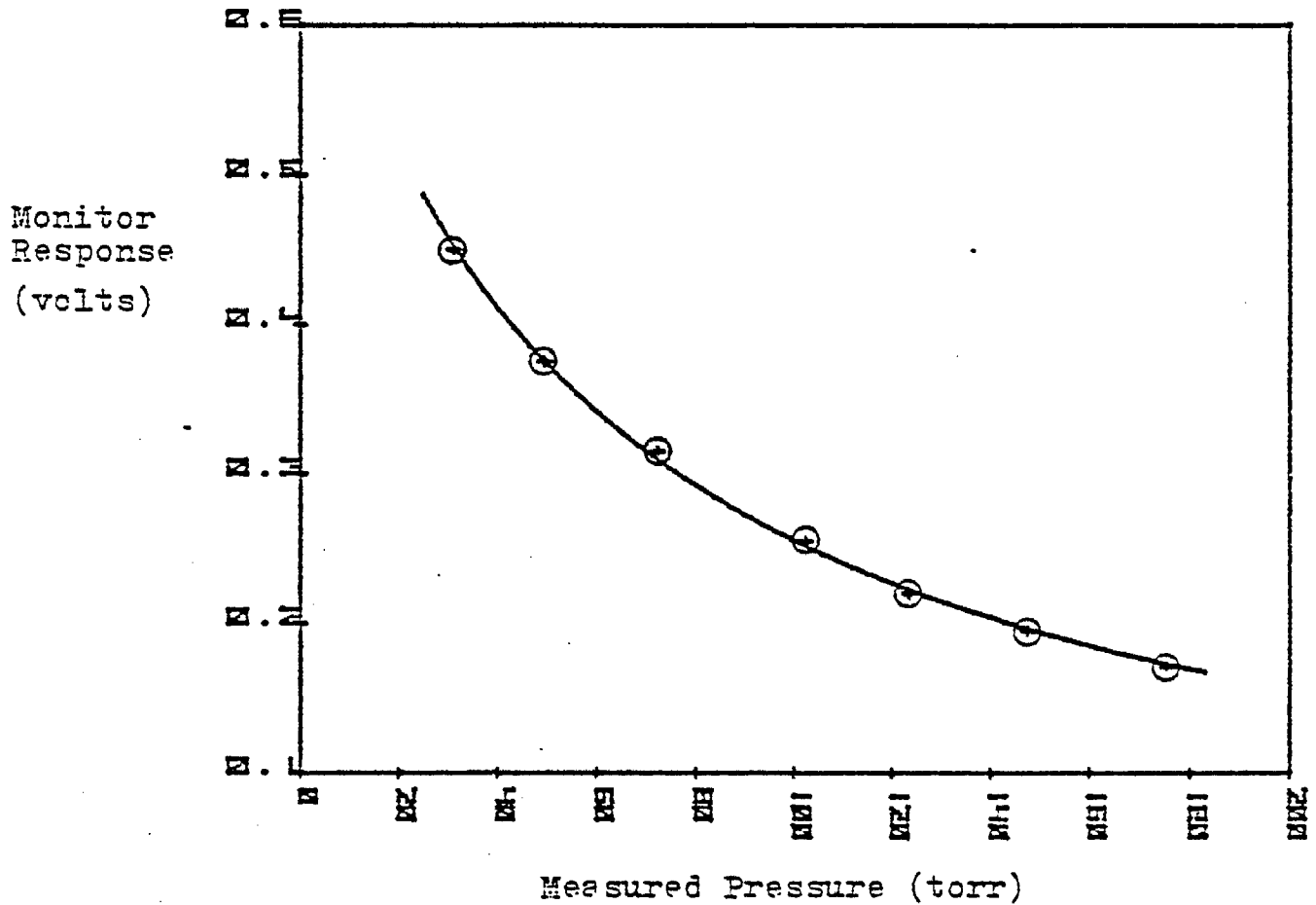


Figure 2-7. Response of a Monitor Labs Model 8440 NO Analyzer to 0.1075 ppm NO as a function of the reactor pressure.



Known concentrations of ammonia were sampled from the output of the ammonia generation and dilution apparatus. The results of the analysis for ammonia desorbed from the Teflon appear in Table 2-3.

From these data, the breakthrough of ammonia appears to occur when the quantity of ammonia collected is about 25 ng. Also, a response of 30 volt-sec for 15 ng of ammonia is not in agreement with the response expected from the steady-state calibration of 136 volt-sec. This indicates that there are significant problems involved with desorption which will have to be resolved before the method can be reduced to practice.

2.6 COMPARISON OF OXALIC ACID FILTER AND THE DIFFUSION DENUDER METHODS

The bubbler method was not accurate at low ammonia concentration and there were significant problems involved with desorption of NH_3 from the Teflon beads; only the oxalic acid and acid coated diffusion denuder methods were selected for comparison. For this, sampling of ambient laboratory air side by side with oxalic acid impregnated filters and diffusion denuder tubes was performed. The results are presented in Table 2-4. There are significant differences between the tubes and the filters. Some stainless steel tubing was on the inlet to the filters and the losses of ammonia by adsorption on this tubing can account for the observed differences.

The average flow used for the diffusion tubes in these experiments was 1.13 ± 0.01 liters/min. The flow rate was measured using a mass flow meter. The collection efficiency of diffusion tubes is a function of the gaseous diffusion coefficient, the tube length, and the volume flow rate. From these parameters, the theoretical collection efficiency is 97%. However, based on the relative quantities of ammonia found in two tubes operated in series, the experimental collection efficiency was calculated to be 77%. Essentially, all the measurements performed with the diffusion tubes have been under conditions in which the tube length and the diffusion coefficient for ammonia have been constant. Therefore, the collection efficiency has varied as a function of

TABLE 2-3. CHEMILUMINESCENT DETECTOR RESPONSE TO AMMONIA
DESORBED FROM TEFLON BEADS AND CONVERTED TO NO

Volume (Liters)	Ammonia Collected \pm Std. Dev. (ng)	Integrated Response (volt-sec)
9.4	126 \pm 4	63.9
6.8	91 \pm 3	51.2
4.5	60 \pm 2	47.4
2.2	30 \pm 1	41.0
1.1	15 \pm .5	30.1

Table 2-4

Comparison of Ammonia Concentrations Measured with the Diffusion Tubes and with Oxalic Acid Impregnated Filters. Standard Deviations Appear in Parenthesis.

<u>Run #</u>	<u>Ammonia from Diffusion Tubes (ppb)</u>	<u>Ammonia from Filters (ppb)</u>
1	17.1 (1.0) 19.5 (1.0) ^a	10.3 (0.5) 9.5 (0.5)
2	17.8 (2.0) 16.7 (1.6)	11.9 (0.6) 12.2 (0.6)
3	20.9 (1.5) 22.8 (1.2)	11.0 (0.5) 5.1 (0.4)

a = the value of 19.5 ppb resulted from a tube that contained a mass of crystals that filled the cross sectional area of the tube. The collection efficiency of this tube was much greater than the others.



the flow rate. A reevaluation of the collection efficiency measurements is given in Table 2-5, and the collection efficiency is plotted as a function of the volume flow rate in Figure 2-8.

One other set of measurements with the diffusion tubes was made in Claremont in conjunction with SAPRC.

Two oxalic acid filter samplers and two diffusion collection devices were installed alongside the Statewide Air Pollution Research Center's (SAPRC) fourier transform long path infrared spectrometer on the roof of the Jacob Science Center at Harvey Mudd College in Claremont, California. Sampling began on Monday, July 23, 1979. Samples were collected from 0900 hours in the morning until 1430 hours in the afternoon, and from 1500 hours in the afternoon until 2030 hours in the evening. This schedule was followed up through Friday, July 27, 1979. Results of the LPIR runs are shown in Table 2-6.

The sampling procedure for LPIR consisted of drawing air into the cell at the rate of 330 liters per second for a minimum of four minutes before the start of an interferometer scan. This corresponded to a displacement of the previous air sample by a minimum of five volumes of fresh sample. A total pathlength of 900 meters and a resolution of 0.5 cm^{-1} were employed. Actual data collection of 30 interferograms took no more than six minutes.

The NH_3 absorption used for analysis is the one at 993 cm^{-1} which has an absorption coefficient of $21 \text{ cm}^{-1} \text{ atm}^{-1}$ (base e) at 0.5 cm^{-1} resolution. The detection limit was typically 4 ppb. The ammonia data from the LPIR has been reduced to give approximately 15 min average ammonia concentrations. These measurements were made by Dr. Ernie Tuazon of SAPRC.

The oxalic acid filter samplers were performed before data concerning the loss of ammonia due to upstream surfaces were available (see Section 3.1.2).



Table 2-5

Evaluation of the Collection Efficiency Measurements
with the Diffusion Denuder Tubes

Sample Flow Rate (l/m)	Measured Collection Efficiency	Theoretical ^a Collection Efficiency	Measurement ^b Method
0.67±0.02	0.98±0.01	0.997	OA backup
1.13±0.01	0.77±0.08	0.970	Tubes in series
4.69±0.08	0.30±0.05	0.631	OA backup

a = theoretical equation from Thomas (21)

b = measured collection efficiency by using oxalic acid impregnated filters
to back up the tubes, i.e. $E_c = \text{NH}_4^+ \text{ on tube} / (\text{NH}_4^+ \text{ on tube} + \text{NH}_4^+ \text{ on filter})$

or by using tubes in series, i.e.

$$E_c = 1 - (\text{NH}_4^+ \text{ on 2nd tube}) / (\text{NH}_4^+ \text{ on 1st tube})$$

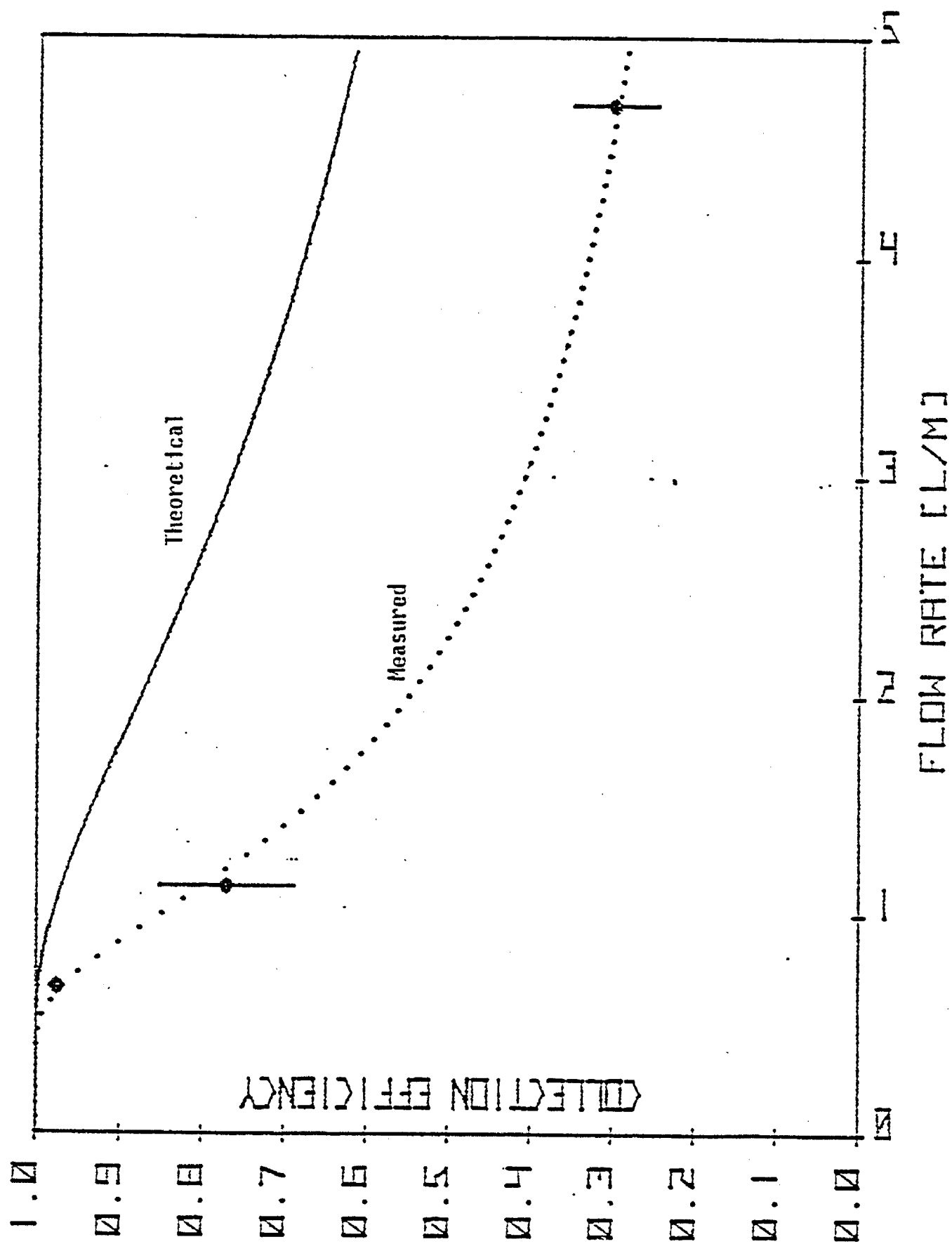


Figure 2-8 Collection efficiency of the diffusion tube method for ammonia gas as a function of the volume flow rate through the tubes. The theoretical curve is based on the equation of the diffusion tube method.

Table 2-7

2-21



Therefore, these data were collected with sampling units that utilized some stainless steel tubing for inlets.

The filters and diffusion tubes collected in Claremont were analyzed and the results are presented in Table 2-7. The amount of ammonium recovered from the diffusion denuder tubes and their after-filters (Teflon) were too low (0.03-0.09 $\mu\text{g/ml}$) to be measured precisely and therefore a great uncertainty is present in their data. The oxalic acid filters, on the other hand, gave ammonium concentrations in the extract at least an order of magnitude greater than that of the diffusion tubes thus securing very precise analytical data. This was because the air flow rate used with the filters is an order of magnitude greater than that used with the diffusion tubes. The ammonium particulate concentrations obtained from prefilters collected in the oxalic acid filter samplers operated side-by-side is plotted in Figure 2-9. Here it can be seen that the precision of the side-by-side sampling is very good. The average deviation in the side-by-side samples is $0.46 \mu\text{g/m}^3$. This deviation represents the total error associated with the sampling and analysis. Converting the units to ppb and including the error associated with the deviation in the blank oxalic acid filters results in the estimated standard error associated with a single ammonia determination of ± 0.4 ppb. Applying this to the ammonia data generated from the oxalic acid filters shows that only 4 out of 9 data pairs are within a standard deviation of 0.4 ppb. Therefore, some random error associated with the ammonia determination by oxalic acid filters is present again in this data. From all the existing data, these random errors can not be associated with errors in the sampling (i.e. flow rates and sample times), contamination of the oxalic acid filter before sampling or low collection efficiency for ammonia. The only possibility that we can presently think of is that the amount measured is real and that the contamination is coming from localized sources that are picked up by one sampler but not the other, which is sitting a few feet away.

As an example, someone may be carrying on a conversation and his breath is picked up by one sampler and not the other. The exhaled breath



TABLE 2-7

Results from the Claremont Experiments (July 1979)

Sample Set	<u>Filters</u>		<u>Tubes</u>	
	(± 0.4 ppb)		(± 0.8 ppb)	
1	6.3	3.8	-	-
2	2.6	2.9	-	-
3	12.2	7.0	5.0	2.4
4	0.8	1.7	1.6	0.3
5	2.6	3.0	1.2	2.0
6	-	-	0	2.6
7	7.3	3.6	1.0	2.2
8	1.4	1.9	3.1	3.0
9	8.4	2.2	-	-
10	1.4	5.0	-	-

Ammonium from Prefilters ($\mu\text{g}/\text{m}^3$)

1	4.89	5.70	-	-
2	6.19	5.77	-	-
3	7.50	7.67	4.86	7.46
4	7.64	7.85	4.65	3.62
5	7.04	7.83	2.42	5.10
6	-	-	7.71	6.88
7	9.83	9.44	6.22	6.59
8	5.53	5.92	5.24	5.93
9	6.37	6.48	-	-
10	6.29	6.37	-	-

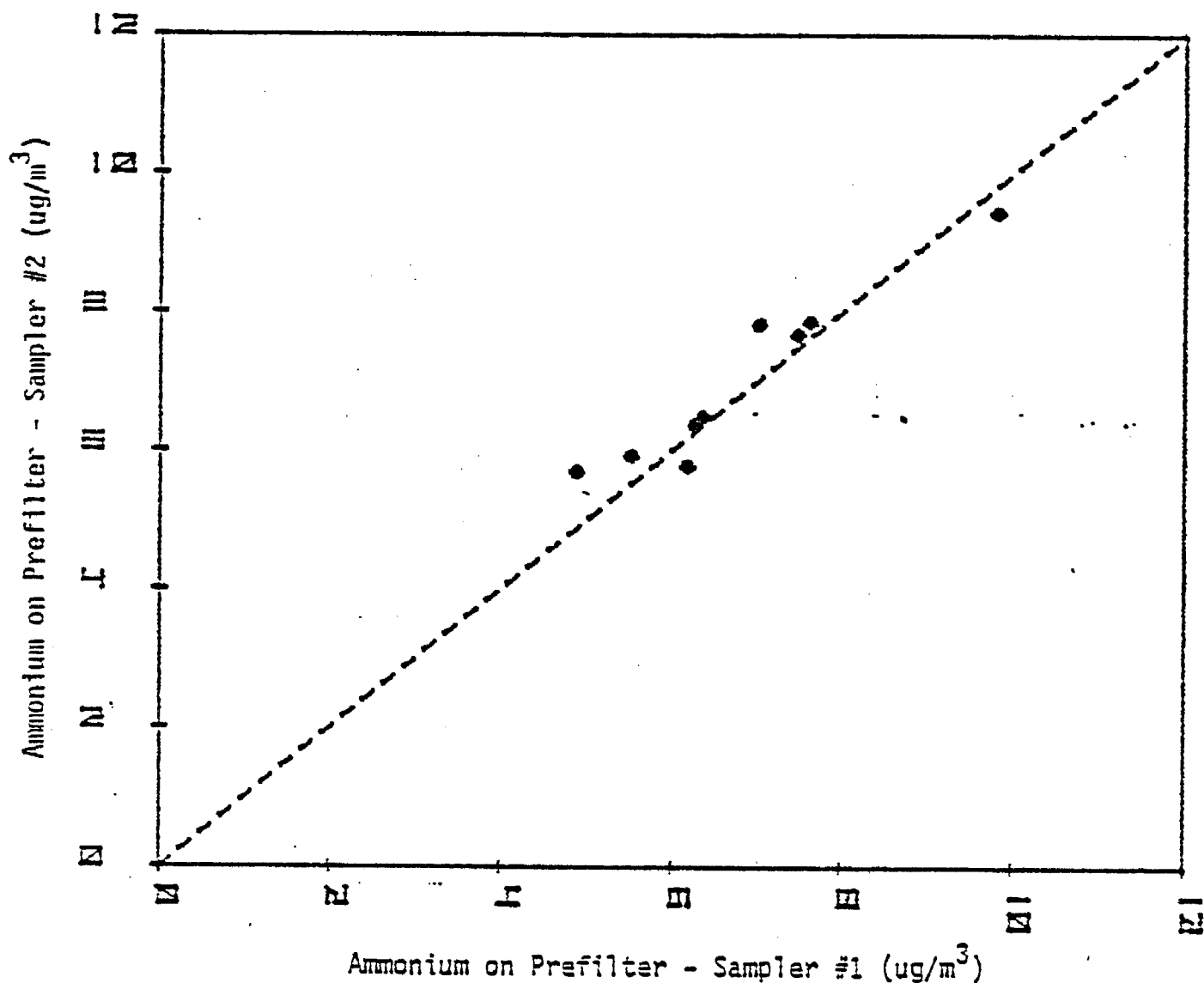


Figure 2-9. Comparison of ammonium particulate found on prefilters collected in identical samplers, sampling side-by-side. Samples collected at Harvey Mudd College in Claremont, California during the period of 7/23 through 7/27/79. The average standard deviation between the data points and the dashed line is 0.46 ug/m³.



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from humans has been measured to contain 300 to 1000 ppb ammonia (Larson, et al. (25)). If 100 ppb of this ammonia is picked up by the one sampler for five minutes out of a four hour sample, the amount determined will be 2 ppb greater than the background. This example indicates that biological contamination during sampling can be critical. At Claremont, there were a number of people in the general vicinity of the ammonia samplers who were working on other projects. It is not inconceivable that what was illustrated above may have occurred. To limit this occurrence, the samplers in the field have been located to minimize the effect of any local ammonia sources (i.e. people).



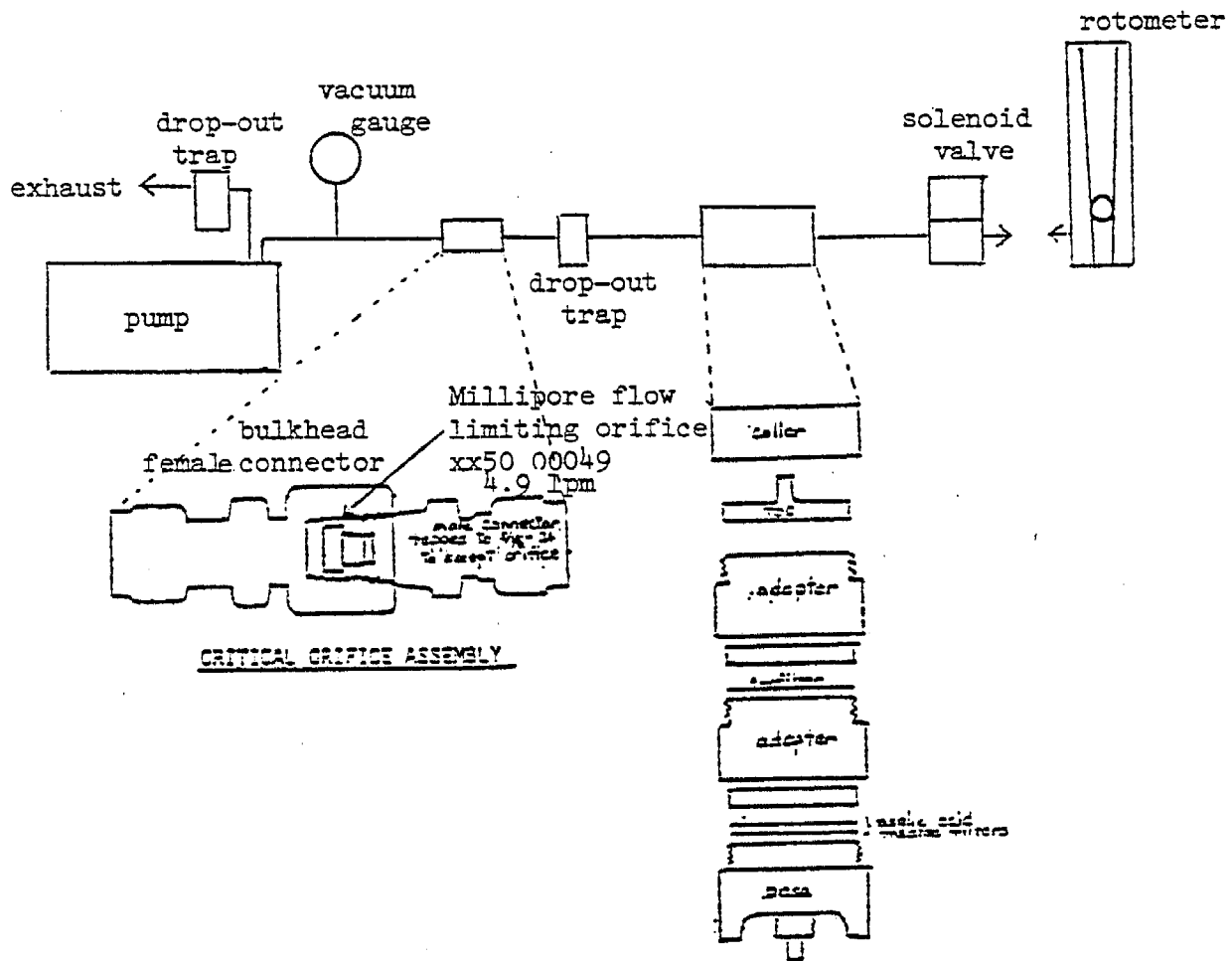
3.0 FIELD SAMPLING

The previously obtained experimental results showed that the oxalic acid filter method gave the most precise analytical data. However, one problem encountered with this method is random contamination from localized source restricting the overall precision for this method to about ± 3 ppb. Considering the average concentration expected near the ocean of 2 to 6 ppb and the concentration measured at Riverside a year ago of 30 to 80 ppb, this method was selected for field monitoring.

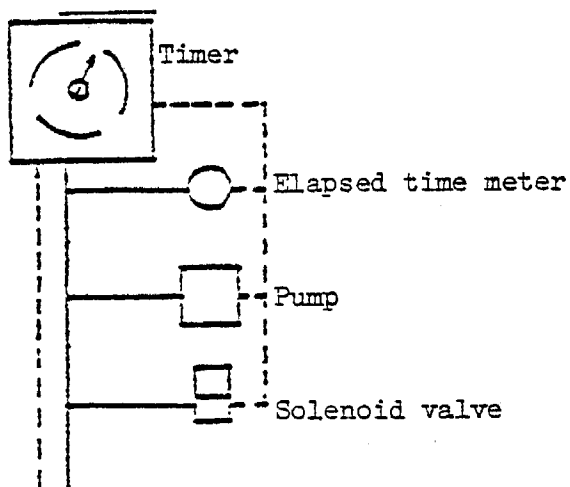
3.1 FIELD SAMPLERS FOR THE OXALIC ACID METHOD

The Rockwell built ammonia sampler consists of a large bore solenoid valve, filter holder, flow orifice, vacuum pump, rotometer, elapsed time meter, vacuum gauge, and timer. The sampler is enclosed in a rainproof aluminum housing. A schematic of the ammonia samplers is depicted in Figure 3-1. The filter material is installed in a Nucleopore 47 mm Swin-Lok multiple filter adapter and holder to provide two stages of filtration, a first stage prefilter and the second stage treated filters for the collection of ammonia. At the end of the sample period the Daylon 7-day timer mechanism disengages the "Skinner" stainless steel solenoid valve and stops the pump. This effectively seals the filter assembly eliminating the loss of sample. Flow is maintained at approximately 4.9 l/min using a Millipore orifice. This acts as a critical orifice at a downstream vacuum of 16 inches of Hg. A drop-out trap prevents plugging of the critical orifice by particulate. A Gast rotary vane vacuum pump provides a vacuum in excess of 20 inches of Hg to meet the above criteria. A Brooks sho-rate 150 rotometer is manually attached to the inlet of the solenoid valve before and after the sample run to establish a start and end sample flow. Measuring the flow before the sample run provides a check for any erroneous flow readings that may result from leaks in the filter holder assembly. These rotometers are calibrated with a Tylan mass flowmeter. Since the Tylan mass flowmeter can be calibrated against an NBS certified positive displacement volume meter (Brooksmeter), the flowrate obtained by these samples can be considered as NBS traceable.

Figure 3.1 PNEUMATIC SCHEME OF AMMONIA SAMPLER



ELECTRICAL SCHEME OF AMMONIA SAMPLER



FILTER HOLDER ASSEMBLY

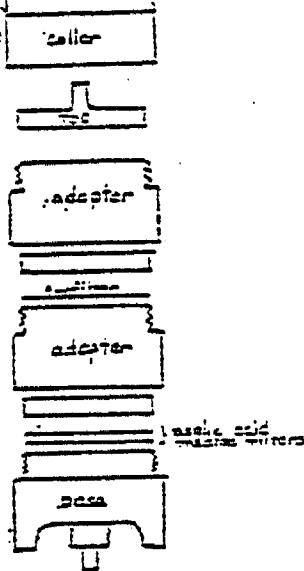




Table 3-1

Calibration of Rotometers in the ARB Ammonia Samplers

	Air Flow Rate @ 760 torr & 25°C (l/m)					
Sampler #	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Float Height (mm)						
20	.794	.801	.827			
40	1.806	1.819	1.851	1.864	1.889	
60	2.909	2.843	2.962	2.935	3.002	
60	2.887	2.849	2.925	2.925	2.963	2.925
80	3.957	3.849	3.993	4.029	4.064	3.939
100	5.041	4.870	5.075	5.143	5.177	4.973
120	6.136	5.909	6.104	6.233	6.266	6.039
Calibration Constants						
A ($\times 10^2$)	-9.9672	-1.6817	1.2193	-7.6540	-2.0523	-23.274
B	19.372	19.727	18.781	18.869	18.437	21.360
C	4.8079	4.1489	4.7108	5.2323	5.2367	-.49765
s_{mm}	.32	.19	.43	.23	.32	.04
$s_{l/m}$.016	.009	.021	.011	.016	.002
r^2	.9999	1.0000	.9999	1.0000	.9999	1.0000

$$Y = Ax^2 + Bx + C$$

Y = Float height in mm

x = Flow rate in l/m.

$$x = \frac{(B^2 - 4A(C-Y))^{1/2} - B}{2A}$$

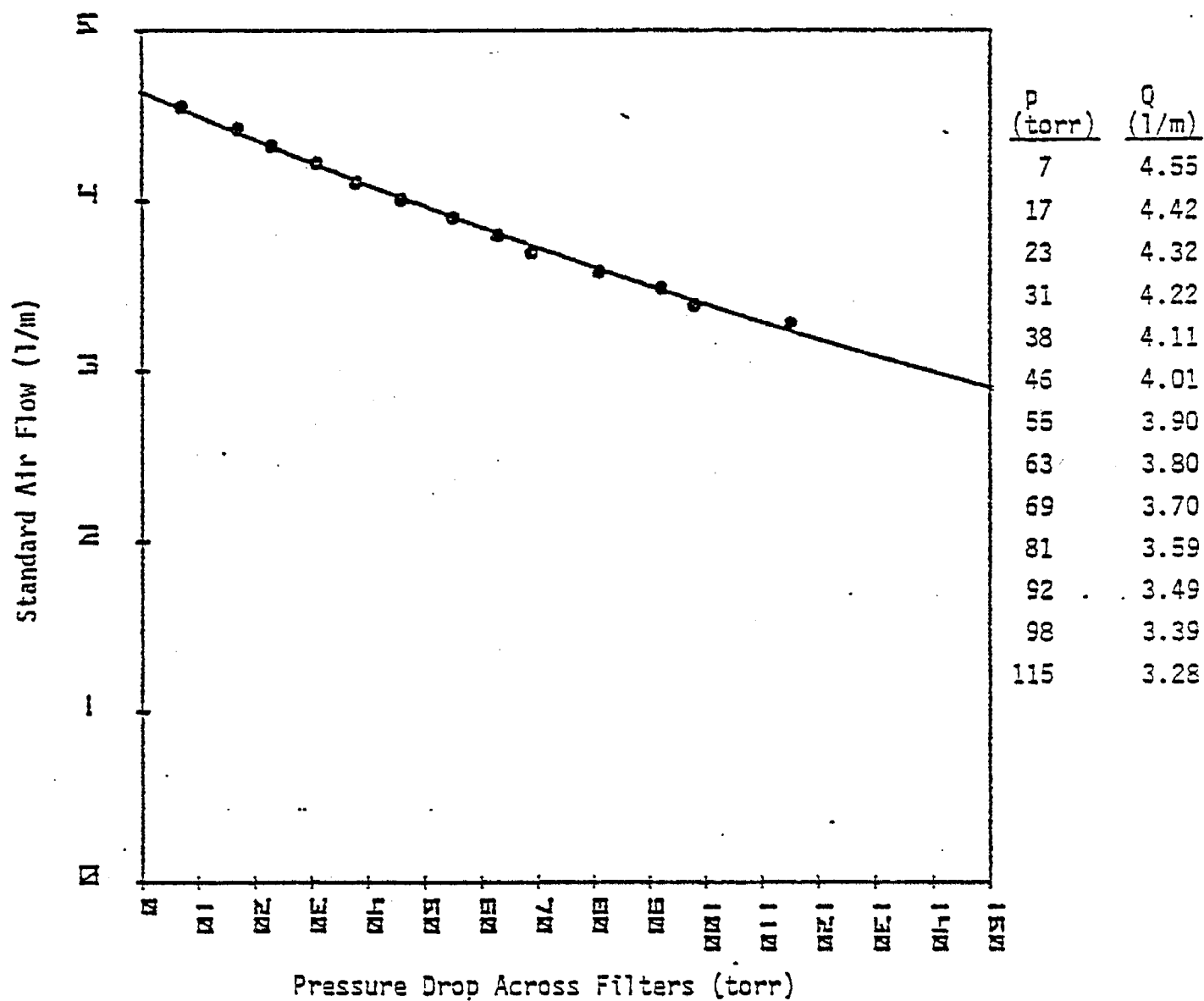


Figure 3-2. Flow rate through the ammonia sampling apparatus as a function of the pressure drop across the sample collecting devices, using a 4.9 l/m critical orifice to control the flow.



Table 3-2

Ammonia Gas and Particulate Ammonium Concentrations Determined by
the Oxalic Acid Filter Method Using Either Teflon or Glass Fiber
Prefilters

Run #	Ammonium Particulate ($\mu\text{g}/\text{m}^3$)		Ammonia Gas (ppb)	
	On Teflon Prefilter	On Glass Fiber Prefilter	On Oxalic Acid Filters with Teflon Prefilter	On oxalic Acid Filter with Glass Fiber Prefilter
1	1.87	1.20	5.8	12.2
	1.75		5.8	
2	2.23	0.42	4.0	7.6
	2.43		5.6	
3	1.77	0.44	10.4	11.1
	2.37		11.1	



- (1) Ammonium in particulates collected on the glass fiber prefilter is released by interaction between the filter and the particulates and is collected as ammonia gas on the oxalic acid filters.
- (2) Ammonia gas is adsorbed by the Teflon prefilter (Teflon is a good adsorbent for ammonia) decreasing the quantity of ammonia gas reaching the oxalic acid filters and increasing the apparent ammonium particulate.

Based on the data available for adsorption of ammonia onto Teflon (McClenny, (12)), it can be very easily calculated that the absorption by the Teflon filter should be much less than 0.01 μg total. Therefore, this and the known alkalinity (Colovos et al. (28)) and reactivity of glass fiber filters (Appel (29); Spicer (30)), implicates process (1) above as being the major contributor to the observed differences in the data.

3.1.2 Evaluation of Ammonia Losses on Upstream Surfaces

Surfaces upstream of the filters include 16" of 1/4" OD stainless steel tubing, a solenoid valve with a 1/4" orifice, and 12" of 1/4" OD polyethylene tubing. To measure the effect of these surfaces, three samplers side-by-side with Teflon prefilters were utilized. One of these three units did have the upstream tubing and valves which offers reactive surface to the incoming air. Table 11 presents the results of these experiments. If run #2 is not considered, the difference between samplers with or without upstream surfaces are very significant. Approximately 54% of the ammonia is collected when upstream surfaces are present. The upstream surfaces also appear to have some effect on the collection of particulate, which can be due to impaction with the tubing wall as the air flows turn corners in the tubing. The amount of sample lost through mass diffusion is negligible.

Losses due to the presence of upstream devices were indicated also in some experiments where samples were collected using the oxalic acid filter and the diffusion denuder methods side-by-side. (This has been discussed in Section 2.6). In these measurements, the oxalic acid samplers did



have the two feet of tubing upstream of the filters. The diffusion samplers did not have anything upstream of the collection devices. The results of this comparison indicated an average concentration determined by the diffusion method of 19.1 ± 2.7 ppb and an average concentration of 11.0 ± 1.1 ppb by the oxalic acid filter method. The ratio of the ammonia concentration by the oxalic acid filter method to the diffusion method is 0.58 ± 0.10 , which is in agreement with the amounts shown in Table 3-3 due to losses involving the upstream surfaces.

The use of some tubing and the solenoid valve upstream of the filters are felt to be necessary to reduce the risk of contamination by ambient ammonia diffusing into the sample holder before the sampling has started and after the sampling has been completed. Polyethylene tubing is used because it is a poor adsorber of ammonia (McClenny (31)), the solenoid valve has a relatively small surface area and probably does not contribute to the losses to any great extent. Therefore, it is felt that most of the losses are occurring in the stainless steel section of the inlet.

3.2 SAMPLING SITES AND FIELD SAMPLING

The field study began August 13, 1979 and ended on May 27, 1980. Additional data were collected by EMSC from June through July 1980.

Six samplers for the oxalic acid method were constructed and were distributed throughout the South Coast Air Basin. Figure 3-3 gives the geographic location of each site.

The sixth sampler was utilized for the collection of duplicate samples and it was colocated with the sampler at each of the five sites for two months. Samples were collected every sixth day (NASN schedule). The routine sampling also involved delivering unexposed oxalic acid filters and prefilters monthly at each of the sites and returning the exposed filters to the laboratory for analysis. Sampling time for each run was 24 hours.



TABLE 3-3

Effects of Reactive Surface with Ammonia Gas

Run #	Ammonia Gas (ppb)		Ammonium Particulate ($\mu\text{g}/\text{m}^3$)	
	Without Upstream Surfaces	With Upstream Surfaces	Without Upstream Surfaces	With Upstream Surfaces
1	5.8	2.4	1.87	1.56
	5.8		1.75	
2	4.0	7.6	2.23	1.71
	5.6		2.43	
3	10.4	7.2	1.77	1.92
	11.1		2.37	

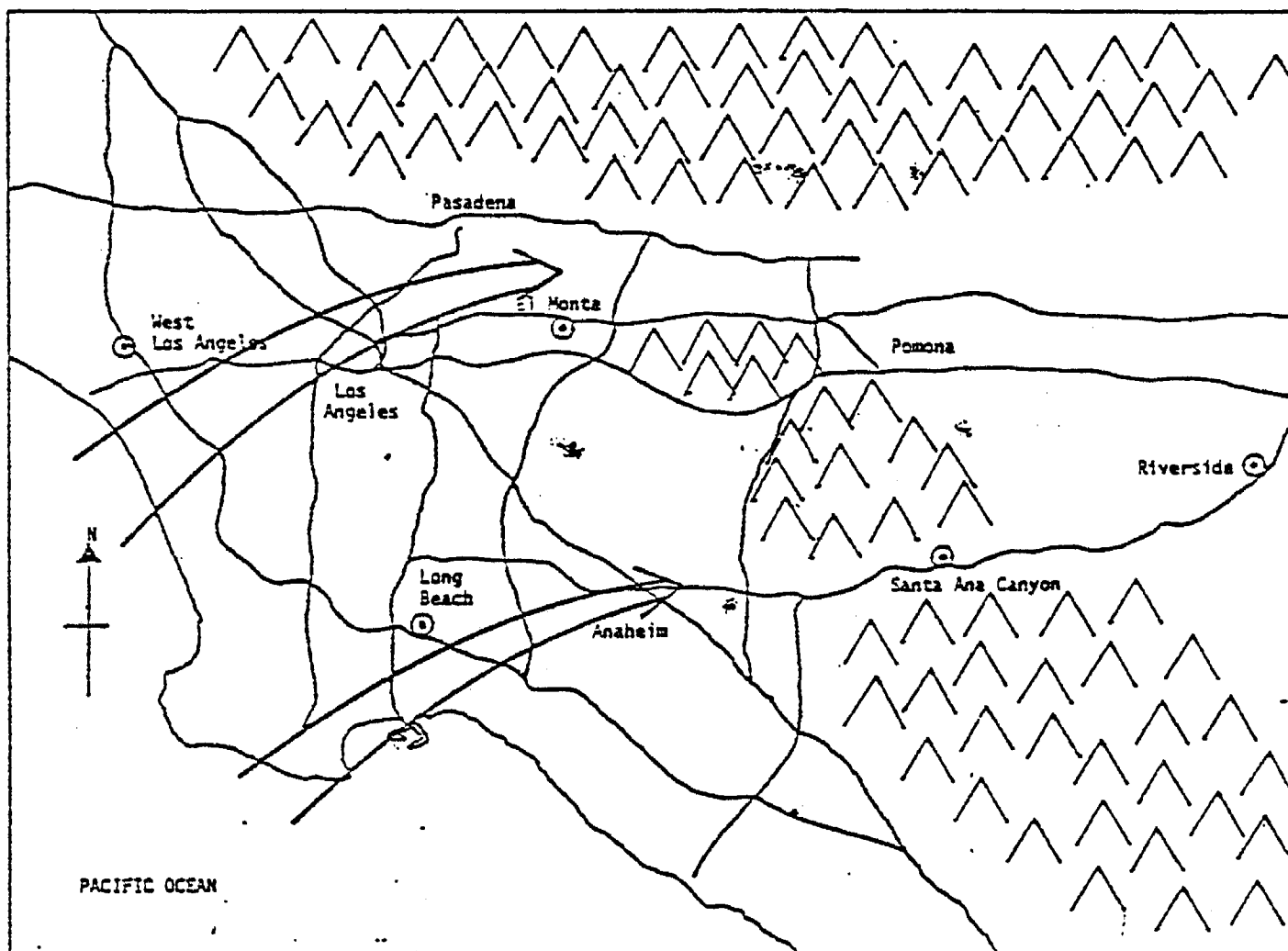


Figure 3-3 Location of Sampling sites in the South Coast Air Basin. Arrows represent prevailing wind trajectories in the mixing layer (Vaughan and Stankunas, 1974).



The sampling sites were:

- West Los Angeles - At the EPA's LACS site, upwind from the San Diego Freeway and downwind from the Pacific Ocean, and approximately 3 to 4 miles of residential communities.
- Long Beach - At the site operated by the South Coast Air Quality Management District (SCAQMD), downwind from major oil refineries, the Long Beach and San Pedro industrial areas, and the San Diego Freeway.
- El Monte - At the ARB's headquarters in El Monte. This site is downwind from metropolitan Los Angeles.
- Santa Ana Canyon - At the site operated by the SCAQMD. The Santa Ana Canyon is a major conduit of the polluted air mass generated in the Long Beach and Orange county areas.
- Riverside - At the ARB's monitoring site in Riverside. This site is downwind from all the major pollution sources in the LA Basin including the dairies in the Chino and Norco areas.



4.0 RESULTS AND DISCUSSION

The results of the field study for all five sites are tabulated in Tables 4-1 through 4-5. These tables show the data of sampling, the ammonia concentration in parts per billion for each of the five sites. Figures 4-1 through 4-5 show the variations of the concentration of ammonia for each site over the sampling period of one year. The monthly ammonia concentration averages for all the five sites are summarized in Table 4-6. These data indicate that of the five sites in the South Coast Air Basin, the concentration of ammonia at West LA site was the lowest ranging from 0.79 ppb to 3.85 ppb. The highest ammonia concentration was at Riverside, ranging from 4.62 ppb to 30.35 ppb. The West LA site is upwind from the San Diego Freeway and downwind from the Pacific Ocean where as Riverside is downwind from all major pollution sources in the LA Basin. The averages for the year at West LA and Riverside were 1.91 ppb and 12.11 ppb respectively. Santa Ana site, a major conduit of the polluted air mass from Long Beach and Orange County had a yearly average of 8.23 ppb of ammonia and a range of 1.42 to 27.65 ppb. Long Beach site which is downwind from major oil refineries, the Long Beach and San Pedro industrial area and the San Diego Freeway has a yearly average of 5.07 ppb of ammonia and a range of 3.09 to 7.93 ppb. El Monte site is downwind from metropolitan LA. It has a yearly average of 4.00 ppb of ammonia and ranging from 1.04 to 8.69 ppb.

From this study it can be concluded that:

1. The oxalic acid method can be used to determine gaseous ammonia concentrations accurately with a precision of about ± 3 ppb;
2. The oxalic acid method can be adapted to monitor gaseous ammonia concentrations in the field as exemplified by the specially constructed samplers; and

Table 4-1

NH₃ CONCENTRATION DATA
FOR THE WEST LA SITE

DATE	NH3 PPB	DATE	NH3 PPB
8/13/79	*****	1/ 4/80	2.66
8/19/79	0.15	1/10/80	2.32
8/25/79	3.88	1/16/80	*****
8/31/79	2.12	1/22/80	4.14
9/ 6/79	1.78	1/28/80	3.12
9/12/79	0.39	2/ 3/80	2.86
9/18/79	3.69	2/ 9/80	1.39
9/24/79	2.37	2/15/80	0.78
9/30/79	1.63	2/21/80	2.35
10/ 6/79	1.98	2/27/80	2.40
10/12/79	0.74	3/ 4/80	2.03
10/18/79	*****	3/10/80	1.35
10/24/79	3.40	3/16/80	9.02
10/30/79	*****	3/22/80	2.99
11/ 5/79	3.81	3/28/80	*****
11/11/79	1.30	4/ 3/80	*****
11/17/79	1.31	4/ 9/80	*****
11/23/79	1.34	4/15/80	1.54
11/29/79	0.80	4/21/80	1.00
12/ 5/79	1.10	4/27/80	1.39
12/11/79	0.37	5/ 3/80	2.18
12/17/79	0.71	5/ 9/80	0.19
12/23/79	1.56	5/15/80	0.43
12/29/79	1.66	5/21/80	0.85
		5/27/80	0.81
		6/ 2/80	0.41
		6/ 8/80	0.52
		6/14/80	0.79
		6/20/80	0.63
		6/26/80	1.58
		7/ 2/80	0.68
		7/ 8/80	0.62
		7/14/80	1.95
		7/20/80	0.32
		7/26/80	1.41

NH3 PPB = CONCENTRATION OF AMMONIA IN PARTS PER BILLION

**** = MISSING OR INVALID DATA

Table 4-2

NH₃ CONCENTRATION DATA
FOR THE LONG BEACH SITE

DATE	NH3 PPB	DATE	NH3 PPB
8/13/79	*****	1/ 4/80	25.93
8/19/79	*****	1/10/80	8.05
8/25/79	*****	1/16/80	7.48
8/31/79	*****	1/22/80	7.03
9/ 6/79	2.52	1/28/80	*****
9/12/79	2.38	2/ 3/80	15.27**
9/18/79	9.16	2/ 9/80	2.63
9/24/79	8.06	2/15/80	10.34
9/30/79	1.11	2/21/80	3.32
10/ 6/79	2.12**	2/27/80	8.07
10/12/79	*****	3/ 4/80	3.98**
10/18/79	2.32	3/10/80	1.81**
10/24/79	6.55	3/16/80	2.60**
10/30/79	2.10	3/22/80	5.14
11/ 5/79	0.06	3/28/80	5.99
11/11/79	*****	4/ 3/80	9.57
11/17/79	3.65	4/ 9/80	5.42
11/23/79	*****	4/15/80	8.40
11/29/79	12.72	4/21/80	*****
12/ 5/79	3.83	4/27/80	1.89
12/11/79	5.23	5/ 3/80	1.78
12/17/79	*****	5/ 9/80	5.38
12/23/79	*****	5/15/80	3.05
12/29/79	*****	5/21/80	2.13
		5/27/80	1.38
		6/ 2/80	1.52
		6/ 8/80	2.08
		6/14/80	1.43
		6/20/80	2.12
		6/26/80	1.86
		7/ 2/80	1.83**
		7/ 8/80	1.59**
		7/14/80	3.69**
		7/20/80	1.75**
		7/26/80	4.38**

NH3 PPB = CONCENTRATION OF AMMONIA IN PARTS PER BILLION

**** = MISSING OR INVALID DATA

Table 4-3

NH₃ CONCENTRATION DATA
FOR THE EL MONTE SITE

DATE	NH3 PPB	DATE	
8/13/79	1.26	1/ 4/80	3.69
8/19/79	2.61	1/10/80	*****
8/25/79	9.21	1/16/80	4.82
8/31/79	10.37	1/22/80	3.34
9/ 6/79	2.78	1/28/80	4.04
9/12/79	6.13	2/ 3/80	5.85
9/18/79	3.70	2/ 9/80	3.64
9/24/79	6.90	2/15/80	3.58
9/30/79	3.40	2/21/80	1.84
10/ 6/79	8.29	2/27/80	6.02
10/12/79	3.31	3/ 4/80	2.95
10/18/79	5.36	3/10/80	3.94
10/24/79	5.74	3/16/80	9.53
10/30/79	2.54	3/22/80	1.01
11/ 5/79	9.90	3/28/80	3.38
11/11/79	7.10	4/ 3/80	3.93
11/17/79	7.74	4/ 9/80	6.33
11/23/79	7.27	4/15/80	3.23
11/29/79	11.44	4/21/80	2.07
12/ 5/79	3.78	4/27/80	1.23
12/11/79	2.27	5/ 3/80	3.51
12/17/79	3.72	5/ 9/80	0.16
12/23/79	3.44	5/15/80	0.49
12/29/79	3.87	5/21/80	0.44
		5/27/80	0.60
		6/ 2/80	0.75
		6/ 8/80	1.55
		6/14/80	2.86
		6/20/80	2.10
		6/26/80	2.99
		7/ 2/80	1.37
		7/ 8/80	0.92
		7/14/80	0.94
		7/20/80	2.35
		7/26/80	2.32

NH3 PPB = CONCENTRATION OF AMMONIA IN PARTS PER BILLION

**** = MISSING OR INVALID DATA

Table 4-4

NH₃ CONCENTRATION DATA
FOR THE SANTA ANA SITE

DATE	NH3 PPB	DATE	NH3 PPB
8/13/79	*****	1/ 4/80	6.98
8/19/79	*****	1/10/80	3.54
8/25/79	*****	1/16/80	2.21
8/31/79	*****	1/22/80	5.56
9/ 6/79	5.08	1/28/80	8.37
9/12/79	4.50	2/ 3/80	6.38
9/18/79	12.27	2/ 9/80	9.25
9/24/79	9.28	2/15/80	20.33
9/30/79	6.11	2/21/80	1.41
10/ 6/79	8.32	2/27/80	8.49
10/12/79	3.89	3/ 4/80	3.78
10/18/79	2.59	3/10/80	11.91
10/24/79	27.68	3/16/80	12.71
10/30/79	9.82	3/22/80	9.70
11/ 5/79	23.74	3/28/80	5.64
11/11/79	20.23	4/ 3/80	5.99
11/17/79	40.74	4/ 9/80	11.93
11/23/79	46.34	4/15/80	4.60
11/29/79	7.18	4/21/80	2.81
12/ 5/79	16.36	4/27/80	1.57
12/11/79	14.14	5/ 3/80	1.47
12/17/79	16.37	5/ 9/80	1.04
12/23/79	3.97	5/15/80	1.86
12/29/79	4.03	5/21/80	2.14
		5/27/80	0.59
		6/ 2/80	1.04
		6/ 8/80	2.83
		6/14/80	1.32
		6/20/80	1.38
		6/26/80	3.99
		7/ 2/80	3.27*
		7/ 8/80	1.62*
		7/14/80	1.59*
		7/20/80	1.76*
		7/26/80	0.80*

NH3 PPB = CONCENTRATION OF AMMONIA IN PARTS PER BILLION

**** = MISSING OR INVALID DATA

Table 4-5

NH₃ CONCENTRATION DATA
FOR THE RIVERSIDE SITE

DATE	NH3 PPB	VWD DEG	VMS MPH	DATE	NH3 PPB	VMD DEG	VMS MPH
8/13/79	10.39	291.	3.7	1/ 4/80	2.44	297.	0.2
8/19/79	11.07	293.	4.5	1/10/80	2.11	252.	2.3
8/25/79	10.49	283.	2.8	1/16/80	30.02	303.	1.1
8/31/79	9.37	283.	3.3	1/22/80	3.31	33.	7.4
9/ 6/79	50.32	298.	3.4	1/28/80	2.48	130.	2.4
9/12/79	14.24	292.	2.2	2/ 3/80	14.93	314.	0.2
9/18/79	15.84	302.	2.0	2/ 9/80	8.24	96.	1.3
9/24/79	12.76	289.	3.3	2/15/80	6.67	61.	1.1
9/30/79	34.07	297.	2.8	2/21/80	5.09	274.	5.7
10/ 6/79	35.66	294.	2.4	2/27/80	11.26	300.	1.3
10/12/79	7.58	289.	1.9	3/ 4/80	9.63	291.	2.2
10/18/79	5.22	278.	1.8	3/10/80	5.19	109.	0.6
10/24/79	28.43	299.	1.5	3/16/80	9.74	8.	4.5
10/30/79	4.13	357.	6.2	3/22/80	9.74	290.	2.2
11/ 5/79	2.83	59.	1.0	3/28/80	8.09	8.	6.7
11/11/79	14.98	309.	0.8	4/ 3/80	8.15	274.	1.7
11/17/79	4.76	285.	2.8	4/ 9/80	10.44	287.	2.2
11/23/79	6.81	305.	1.4	4/15/80	10.35	293.	2.0
11/29/79	3.78	64.	6.6	4/21/80	2.89	283.	4.2
12/ 5/79	1.78	12.	8.6	4/27/80	14.27	281.	3.0
12/11/79	1.85	27.	9.6	5/ 3/80	10.15	288.	3.3
12/17/79	10.60	108.	0.5	5/ 9/80	2.50	294.	5.8
12/23/79	9.88	288.	0.4	5/15/80	3.64	290.	2.7
12/29/79	2.23	110.	2.0	5/21/80	3.41	290.	4.5
				5/27/80	3.40	287.	3.2
				6/ 2/80	9.88	293.	3.1
				6/ 8/80	11.18	287.	2.7
				6/14/80	8.97	296.	2.8
				6/20/80	12.51	287.	3.1
				6/26/80	14.93	290.	2.6
				7/ 2/80	26.62	*****	
				7/ 8/80	23.41	*****	
				7/14/80	13.67	*****	
				7/20/80	37.66	*****	
				7/26/80	50.40	****	

NH3 PPB = CONCENTRATION OF AMMONIA IN PARTS PER BILLION

**** = MISSING OR INVALID DATA

Figure 4-1. Concentration of NH_3 (ppb) West LA

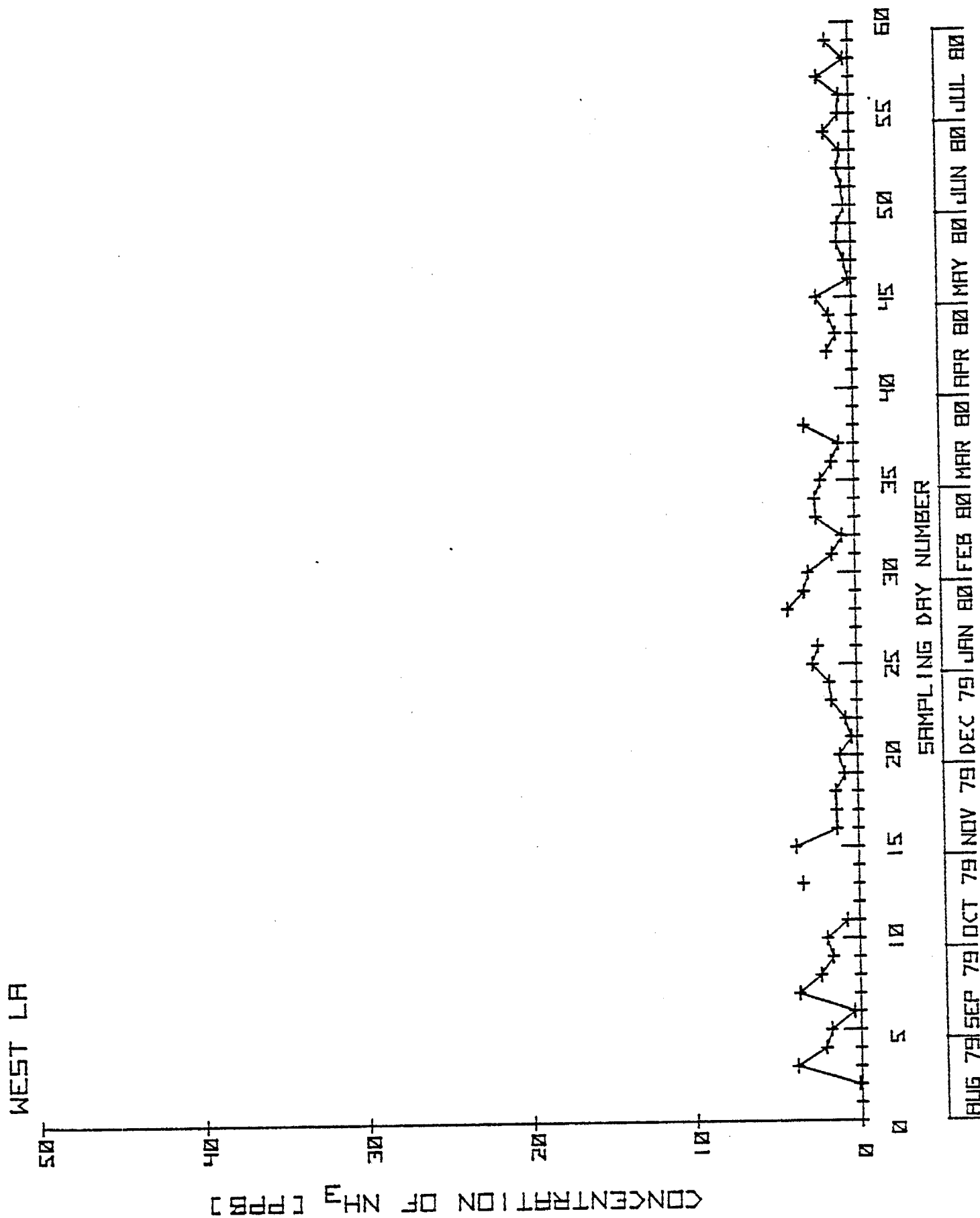


Figure 4-2. Concentration of NH_3 (ppb) Long Beach

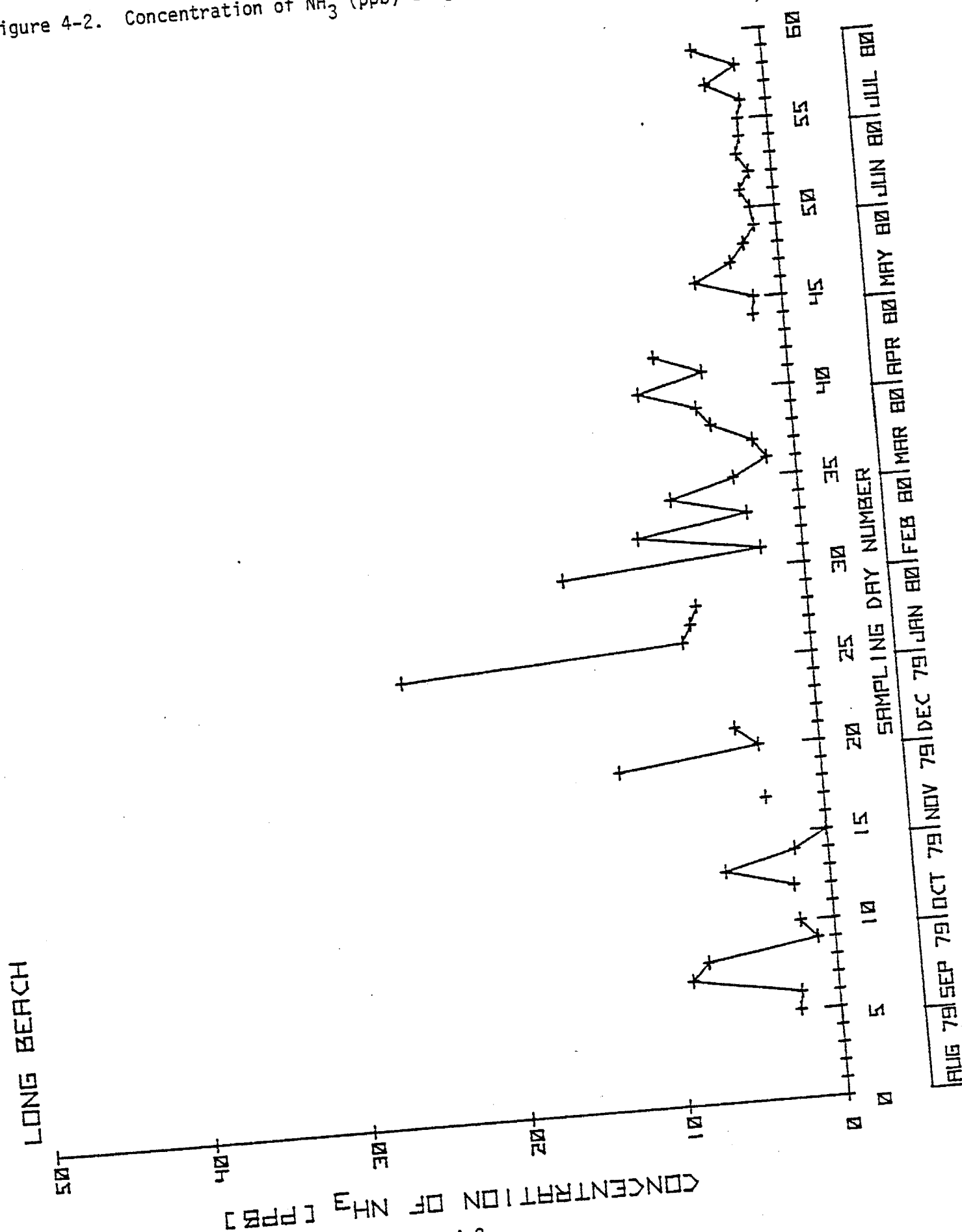


Figure 4-3. Concentration of NH_3 (ppb) El Monte

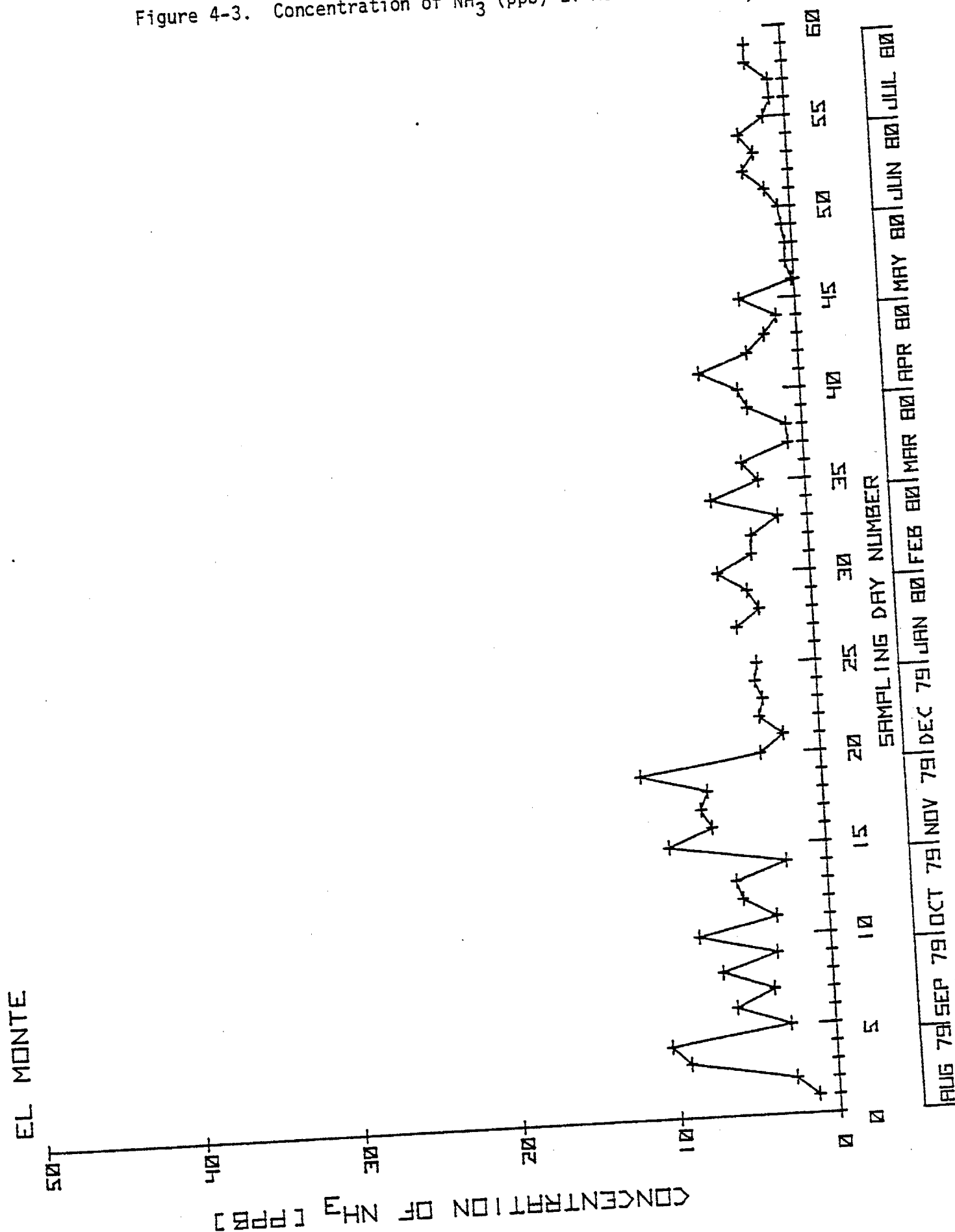


Figure 4-4. Concentration of NH_3 (ppb) Santa Ana

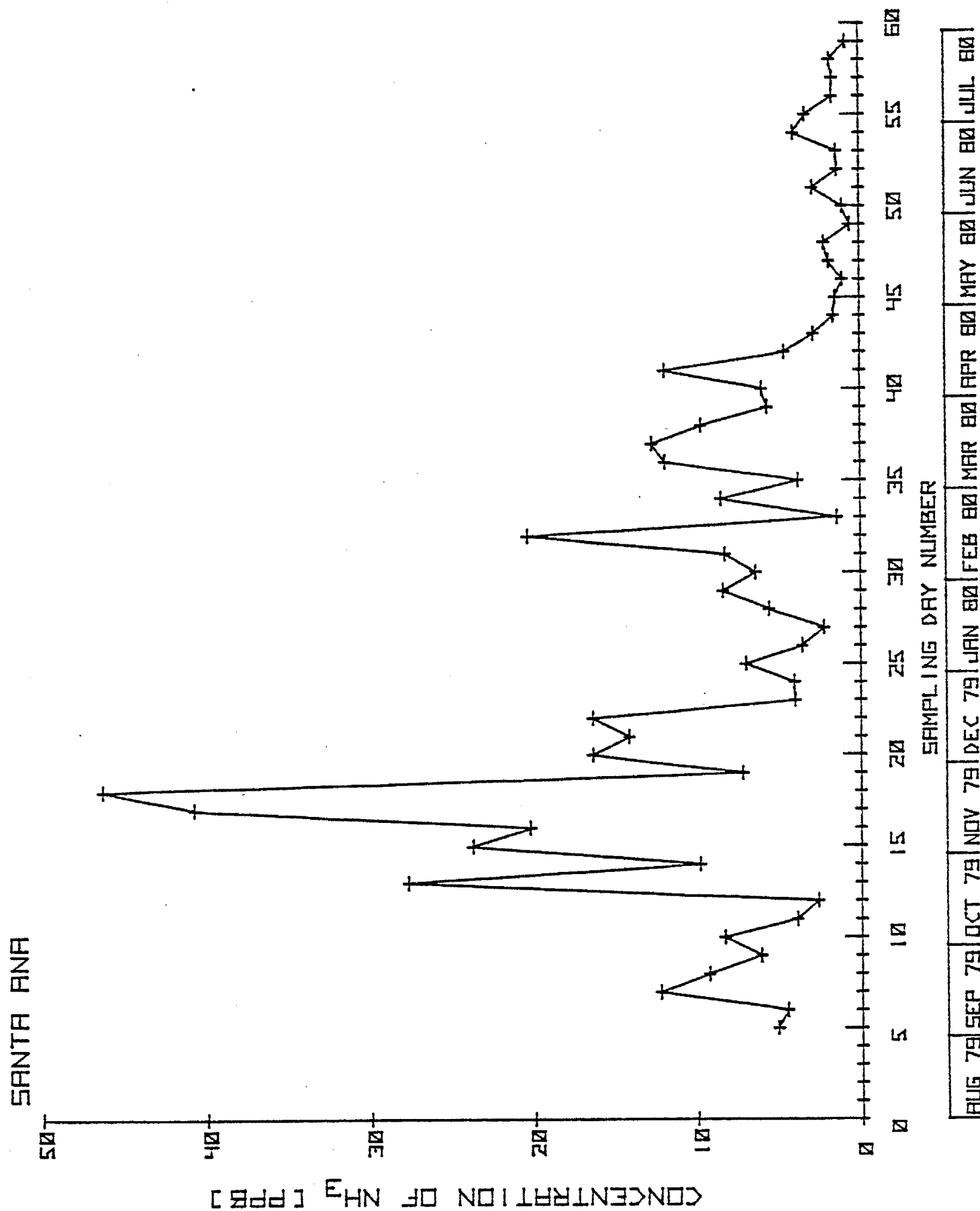


Figure 4-5. Concentration of NH_3 (ppb) Riverside

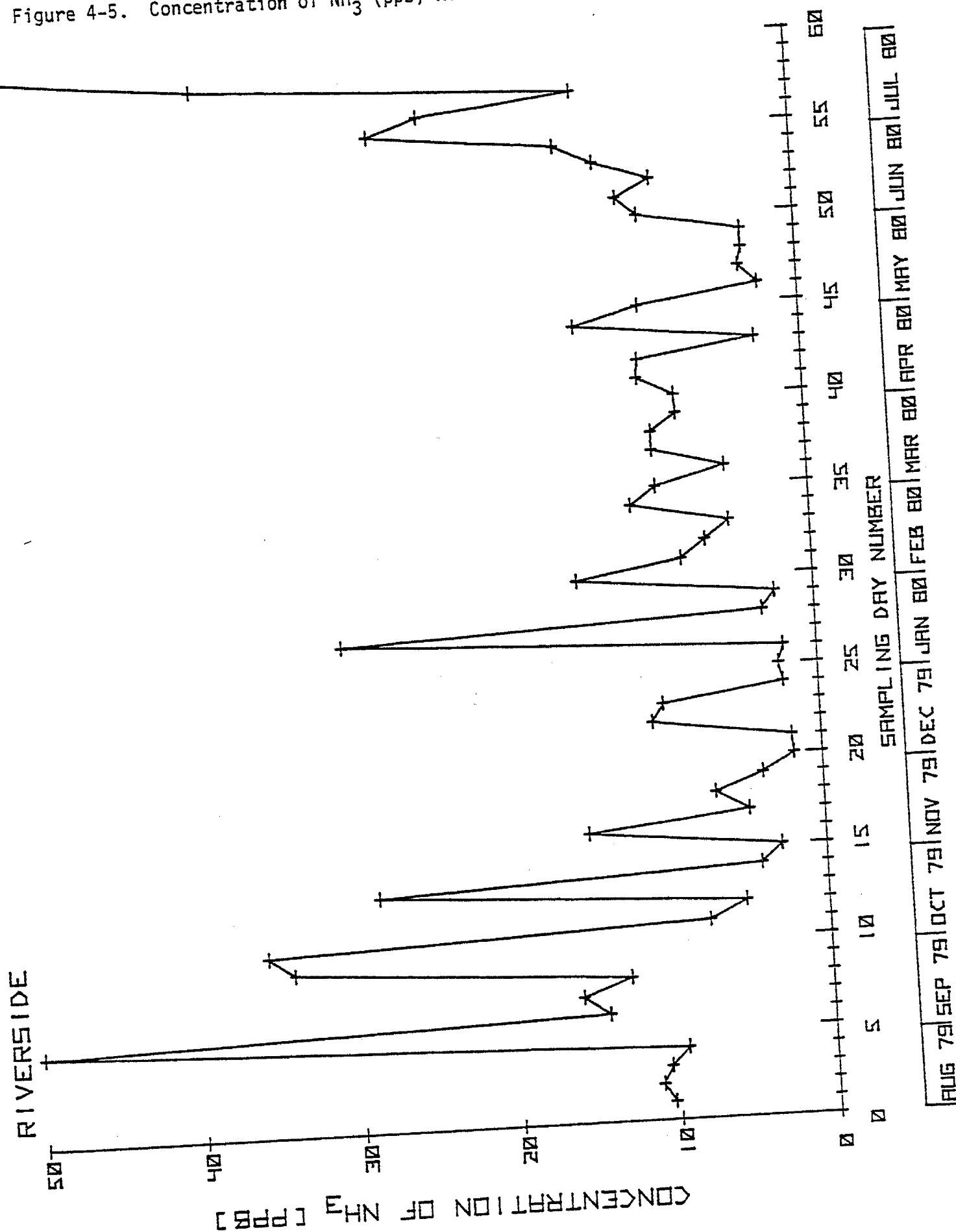




TABLE 4-6

Monthly and Annual Ammonia Concentration (ppb)
Averages* for the South Coast Air Basin

	W.LA	LONG BEACH	EL MONTE	SANTA ANA	RIVERSIDE
Aug	2.05	--	5.86	--	10.33
Sep	1.97	4.65	4.58	7.45	25.44
Oct	2.04	3.27	5.05	10.46	16.20
Nov	1.71	5.48	8.69	27.65	6.63
Dec	1.08	4.53	3.42	10.97	5.27
Jan	3.06	12.12	3.97	5.33	8.07
Feb	1.96	7.93	4.19	9.17	9.24
Mar	3.85	3.90	4.16	8.75	8.48
Apr	1.31	6.32	3.36	5.38	9.22
May	0.89	3.09	1.04	1.42	4.62
Jun	0.79	1.80	2.05	2.11	11.49
Jul	1.00	2.65	1.58	1.81	30.35
Annual Ave.	1.81	5.07	4.00	8.23	12.11

* Monthly and annual averages were calculated from the data obtained every sixth day (NASN schedule) and averaged over number of sampling days for the month or year respectively.



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3. The results of the field studies indicate annual average ammonia concentrations in West Los Angeles, Long Beach, El Monte, Santa Ana, and Riverside are 1.81, 5.07, 4.00, 8.23 and 12.11 ppb, respectively.



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